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The Degradation of Tall Oil Fatty Acids by Molecular Oxygen in Alkaline Media

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THE DEGRADATION OF TALL OIL FATTY ACIDS BY MOLECULAR OXYGEN IN ALKALINE MEDIA

A thesis submitted by

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SUMMARY

The reactions of tall oil fatty acids and their esters with molecular oxygen and alkali were investigated under conditions chosen to simulate those which might be encountered in an oxygen-alkali delignification process. The primary objective of the investigation was to determine those reaction conditions most compatible with recovery of the fatty acids. Another objective, complementary to the first, involved identification of the fatty acid oxidation products and measurements of their yields. The product analyses were intended to account for the fatty acid losses which did occur, and to obtain some understanding of the fatty acid oxidation mechanisms.

To satisfy the primary objective, a half factorial experimental design involving sixteen reactions was developed to investigate the relative effects of five variables on the degradation of two fatty acid esters, methyl oleate and methyl linoleate. The variables considered were temperature, reaction time, oxygen pressure, alkali and substrate. The magnitudes of the first three parameters were varied, while the alkali variable was represented by either sodium hydroxide or an equimolar amount of sodium bicarbonate. The substrate variable, which consisted of either preextracted loblolly pinewood meal or cotton linters, was included to investigate the "protective effect" of wood on oxidation of the fatty acid esters. The two substrates differed most significantly in their lignin contents, since the protective effect was interpreted as a possible antioxidant property of lignin derived phenols.

To facilitate identification of fatty acid oxidation products, the methyl esters and sodium soaps of pure oleic acid and linoleic acid were oxidized. Their reaction products were analyzed by combined gas chromatography-mass spectrometry. The reactions of four saturated fatty acids possessing from sixteen to twenty-two carbon atoms were also briefly investigated.

However, the saturated fatty acids and their esters were very resistant to reaction with oxygen-alkali, and none of their oxidation products were detected.

Effects of the reaction variables on fatty acid degradation were determined from the yields of unreacted starting material measured in all reactions associated with the half factorial experimental design. Raising the temperature from 100 to 160°C increased oxidation of the fatty acid esters to about the same extent as extending the reaction time from 2 to 8 hours. Increasing the oxygen pressure from 690 to 3500 kPa also resulted in more extensive fatty acid oxidation. However, the effect of this variable was dependent on the nature of the substrate. Although oxygen pressure had a significant effect in reaction systems containing wood meal, its effect was negligible in systems containing cotton linters. Alkali exerted by far the most pronounced effect of any variable considered. Much more extensive degradation of both fatty acid methyl esters and free fatty acids was promoted by the weaker base, sodium bicarbonate. The possible participation of carbonate radicals was considered to explain the observed result. The effect of substrate was markedly influenced by the alkali. Wood meal did exhibit a protective effect when fatty acids or their esters underwent reaction with sodium bicarbonate and oxygen, and that effect was lost when the bicarbonate was replaced with hydroxide.

Distributions of the fatty acid oxidation products were also dependent upon the reaction conditions. The identified oxidation products generally accounted for between 30 and 40% of the starting material consumed. However, small quantities of numerous other compounds were detected by gas-liquid chromatography. The remainder of the lost matter was assumed to consist of those compounds and other low molecular weight oxidation products. Carboxylic acids, dicarboxylic acids and long chain hydroxy acids were found among the products of almost all reactions. α-Hydroxy mono- and dibasic-carboxylic acids were

other major products, but only of reactions conducted in aqueous sodium hydroxide solutions, or carried out in the presence of both sodium hydroxide and cotton linters. Formation of the α-hydroxy acids was therefore promoted by strong alkali. Those compounds were not significant products of any reactions conducted with sodium bicarbonate, nor were they formed in appreciable quantities if the reaction system contained wood meal and sodium hydroxide. Other important compounds found among the products of all sodium bicarbonate based reactions were ω-hydroxy acids. The oxidation reactions were more selective at low temperature than at high temperature. Cleavage of the fatty acid molecules at or near the locations of their double bonds was preferred at 100°C, while complex mixtures of reaction products containing many low molecular weight compounds were obtained at 160°C. Hydroperoxides were not identified; such compounds were the presumed primary products of fatty acid autoxidation. Different hydroperoxide decomposition pathways were considered to account for formation of the observed products. Several intermediate reaction products were identified which provided additional evidence for the reaction mechanisms suggested.

The results of this investigation indicate that recovery of tall oil fatty acids will not be possible in an oxygen-bicarbonate delignification process without some type of pretreatment, such as alkaline extraction. Although the naturally occurring fatty acid esters will not be saponified in systems containing oxygen and bicarbonate, they are likely to undergo extensive oxidation degradation. Conditions most favorable to fatty acid recovery during oxygen-alkali delignification include low temperature, short reaction time and strong alkali; a high pH should be maintained if recovery of the fatty acids is desired. Oxidation of the fatty acids and their esters results in the formation of many potentially valuable acidic oxidation products; yields of individual compounds are generally very low, and their recovery from spent liquor would be difficult.

THESIS OBJECTIVES

This thesis was conceived to investigate the reactions of tall oil fatty acids under conditions simulating those of oxygen-alkali delignification. The methyl esters or sodium soaps of oleic acid, linoleic acid and several saturated fatty acids were the compounds investigated.

An experimental program designed to determine the effects of temperature, reaction time, oxygen pressure, alkali, and lignin content on the autoxidation of methyl oleate and methyl linoleate was developed. The primary purpose of the program was to define conditions least likely to promote degradation of tall oil fatty acids during delignification of wood or pulp with oxygen and alkali.

Another important goal of the experimental program was to account for the losses of the fatty acid esters which did occur. This objective required identification of fatty acid oxidation products and measurements of their yields. This phase of the investigation was intended to explore the possibility of recovering potentially valuable oxidation products and to clarify the mechanism of fatty acid degradation by oxygen and alkali.

INTRODUCTION

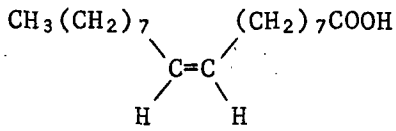
Because of environmental problems associated with the kraft pulping process, alternate pulping methods have been devised. One of the more promising alternatives is delignification with oxygen and alkali. However, the viability of tall oil and turpentine recovery, which is an important advantage of the kraft process, has not been adequately explored in research on oxygen-alkali delignification.

Among the extractives of wood, three classes of compounds comprise the commercially important by-products of kraft pulping. They are monoterpenes, diterpene resin acids, and fatty acids. Monoterpenes constitute the major fraction of sulfate turpentine, while the resin and fatty acids are recovered from kraft black liquor as tall oil soap. The probable reactions of extractives during oxygen-alkali delignification were discussed by Hrutfiord and Hopley (1). They predicted that autoxidation of the extractive components would result in decreased yields of both tall oil and turpentine. Tall oil yields from thermomechanical pulp treated with oxygen and sodium hydroxide were measured by Erickson and Dence (2), while Pearl and Dickey (3) compared the yields of tall oil obtained after kraft, soda and soda-oxygen pulping of pinewood chips. In each case tall oil recovery after treatment with oxygen was substantially reduced from that which could be achieved by the kraft process. Presumably, the fatty and resin acids underwent oxidative degradation during delignification. However, Pearl and Dickey (3) also demonstrated that considerable quantities of tall oil components remained in soda and soda-oxygen pulps after they were washed with water. Similarly, Pusa and Virkola (4) found that substantial quantities of extractives remained in sulfite pulp after treatment with oxygen and sodium hydroxide.

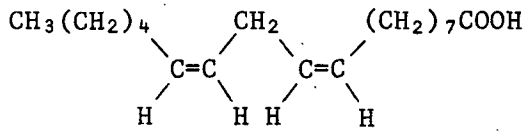
Evidence suggests that tall oil acids are at least partially degraded by oxygen and alkali. No attempts have been made to determine the conditions of oxygen-alkali delignification which might be most conducive to tall oil recovery. Furthermore, no satisfactory account has yet been made of the tall oil components which are consumed during delignification. This thesis, which is concerned specifically with the reactions of tall oil fatty acids, addresses both of those questions.

FATTY ACIDS OF SOUTHERN PINEWOOD

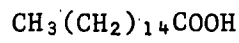
Tall oil fatty acids occur in wood predominately as triglyceride esters, with lesser quantities as sterol esters or waxes. The two most abundant fatty acids are oleic acid (cis-9-octadecenoic acid) and linoleic acid (cis,cis-9,12-octadecadienoic acid). In loblolly pinewood these two unsaturated compounds



Oleic Acid



Linoleic Acid



Palmitic Acid

are found in approximately equal quantities and together account for about 80% of all the fatty acids (5). The third most abundant fatty acid is palmitic acid (hexadecanoic acid), a saturated acid which accounts for about 6% of all fatty acids in loblolly pine. The remaining fatty acids are saturated and unsaturated compounds of varying chain lengths and varying degrees of unsaturation.

AUTOXIDATION OF FATTY ACIDS

All of the fatty acids found in wood are susceptible to reactions with the molecular oxygen present in air; under ambient conditions such reactions are commonly termed autoxidations. Hereafter, autoxidation will refer to any

reaction involving molecular oxygen. Olefin autoxidation was the subject of extensive research conducted under the direction of the British Rubber Producers Research Association. The kinetics and mechanism of autoxidation were elucidated during those investigations, and the results have been discussed in reviews by Bolland (6) and by Bateman (7). The mechanism of autoxidation which was proposed at that time, and which is still generally accepted, is represented by Equations (1) through (6).

Initiation	$RH + I \text{ (Initiator)} \longrightarrow R\cdot + IH$	(1)
Propagation	$R\cdot + O_2 \longrightarrow ROO\cdot$	(2)
	$ROO\cdot + RH \longrightarrow ROOH + R\cdot$	(3)
Termination	$R\cdot + R\cdot \longrightarrow$ "Inert"	(4)
	$R\cdot + ROO\cdot \longrightarrow$ Products	(5)
	$ROO\cdot + ROO\cdot \longrightarrow$	(6)

The mechanism outlined is a radical chain reaction. Autoxidation may be initiated by any species which will induce cleavage of carbon-hydrogen bonds. Common initiators include free radicals and ultraviolet light. In the first step of the sequence a hydrogen atom is abstracted by the initiating species, yielding a chain-propagating free radical (R•). An allylic hydrogen atom is usually abstracted preferentially from unsaturated compounds, since the resulting free radical is resonance-stabilized. The free radical rapidly combines with oxygen to produce a peroxy radical as shown in Equation (2). The peroxy radical abstracts a hydrogen atom from a second reactant molecule, yielding another reactive free radical and a hydroperoxide, as represented by Equation (3). Reactions (2) and (3) are defined as chain-propagating steps, since in each case a radical is formed which may directly or indirectly initiate further oxidation. Under mild conditions hydroperoxides are the end products of autoxidation, which is terminated when the free radicals decompose to form products incapable of initiating or propagating further reaction, as indicated by

Equations (4)-(6). For autoxidation, the chain length is defined as the number of times Reactions (2) and (3) will occur before the sequence is interrupted by a termination reaction. At relatively high oxygen pressures the rates of the termination steps, (4) and (5), become insignificant compared to the rate of propagation step, (3), and termination occurs almost exclusively by Reaction (6). Under suitable reaction conditions, and in the absence of pro- or antioxidants, autoxidation may be characterized by long chain lengths and high yields of hydroperoxides.

The autoxidation of fatty acids and fatty acid derivatives may also be described by the general mechanism of autoxidation shown in Equations (1) through (6). In fact, esters of oleic acid and linoleic acid were commonly used as model compounds in many of the studies dealing with general olefin autoxidation. Numerous investigations by many different groups of workers have been directed specifically to the autoxidation reactions of fats and oils. Most of this work was undertaken to clarify the chemistry associated with the development of rancidity in cooking oils and the polymerization of drying oils. In most instances, the initial stages of autoxidation were adequately described by the radical chain mechanism. Research dealing with the autoxidation of fats and oils has been reviewed by Holman (8), Swern, et al. (9), and Swern and Coleman (10).

METHYL PALMITATE

While all fatty acids are subject to reaction with oxygen, saturated fatty acids are autoxidized very slowly unless relatively severe conditions are imposed. Since such compounds do not contain double bonds, the oxidations are not as specific as analogous reactions involving unsaturated compounds. Hydroperoxide formation during autoxidation of methyl palmitate was investigated by Brodnitz,

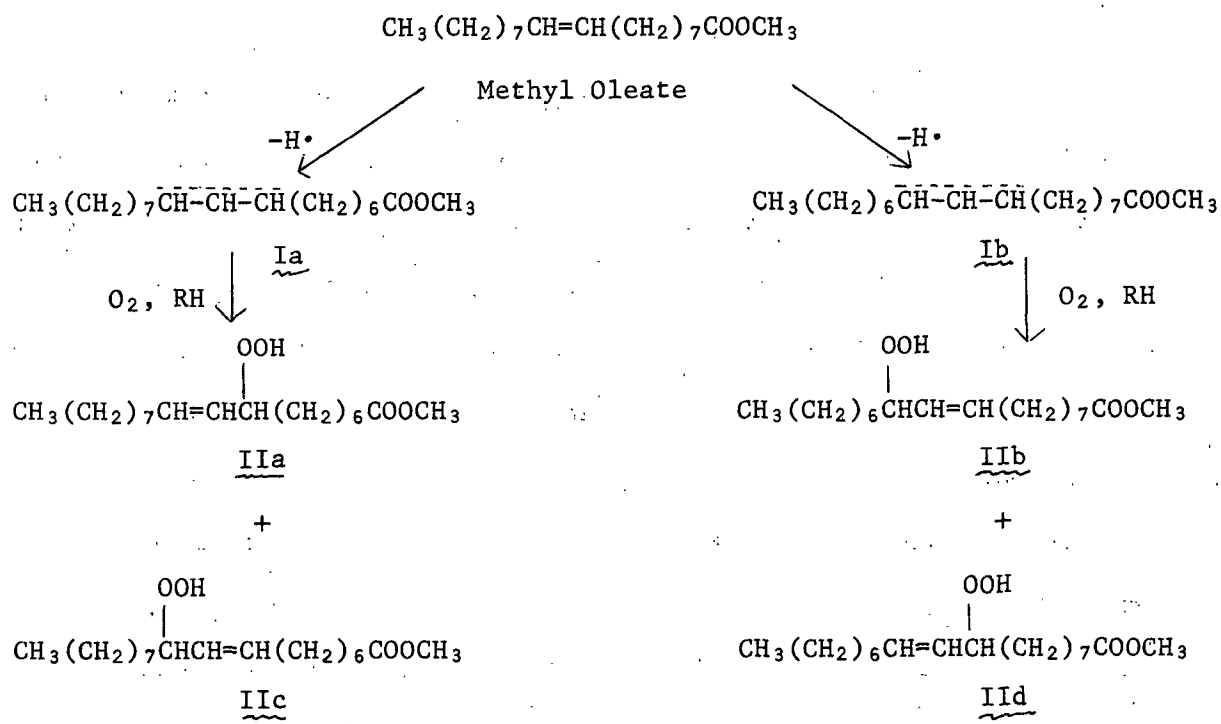
et al. (11). The ester was heated to 150°C in air, and an analysis of the

$$\underset{\text{Methyl Palmitate}}{CH_3(CH_2)_{14}COOCH_3} \xrightarrow{O_2} \text{Numerous Monohydroperoxides}$$

resulting mixture of hydroperoxides was attempted. The results indicated that monohydroperoxides were the primary products. Although oxidation appeared to occur preferentially toward the center of the molecule, the initial attack by oxygen was not favored at any particular site.

METHYL OLEATE

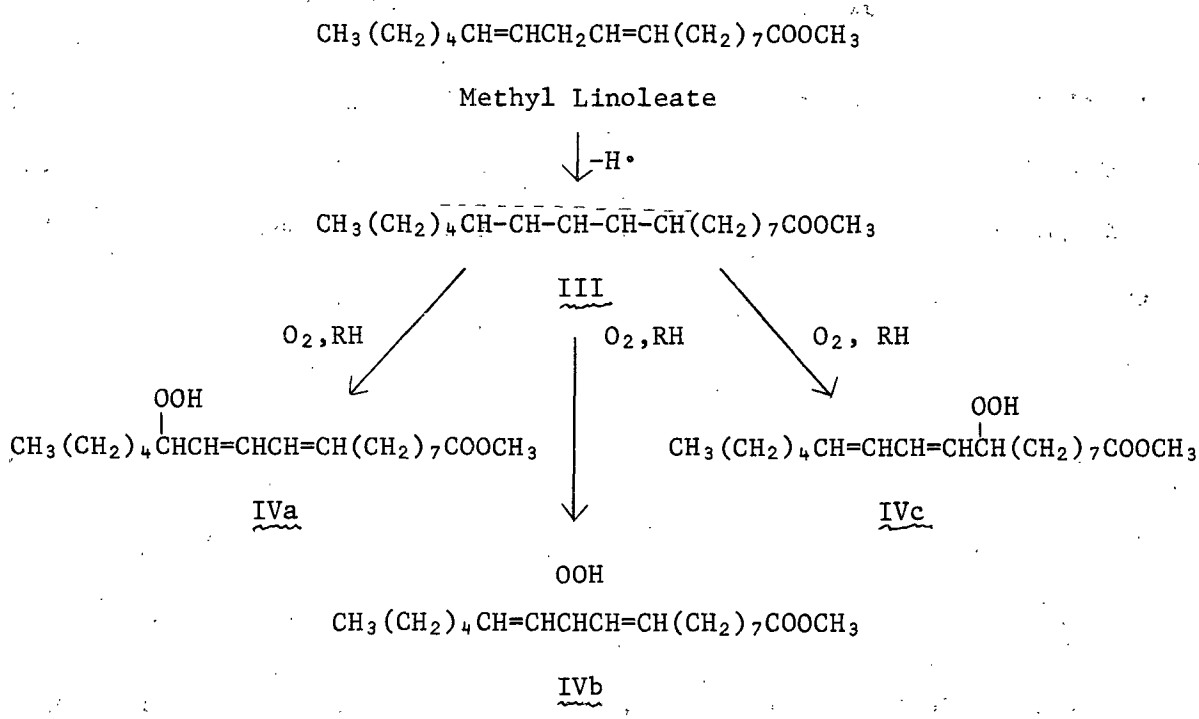
Methyl oleate possesses two allylic methylene groups, either one of which may lose a hydrogen atom to an initiating free radical. Two different resonance-stabilized allylic free radicals may thus be formed (Ia, Ib), and each of them may combine with oxygen at two different sites. In methyl oleate, hydroperoxide



formation may occur at any one of the four carbon atoms part of, or adjacent to, the original double bond. Furthermore, each of the four probable hydroperoxides, the general structures of which are shown (IIa-IId), has two geometric isomers. Structural determinations of the hydroperoxides obtained from autoxidized methyl oleate have been the objects of several recent investigations (12-14). Although this aspect of autoxidation was also of considerable interest in earlier work (8-10), analytical techniques had not been developed which permitted unequivocal identifications of individual hydroperoxides. All eight of the predicted hydroperoxides were identified by Garwood et al. (12) when methyl oleate was autoxidized at temperatures ranging from 25 to 75°C. The four positional isomers were found in approximately equal quantities at all temperatures. However, the hydroperoxides tended to assume trans configurations, particularly in those compounds (IIb,IId) whose formation coincided with migration of the double bond. Similar results were reported by Capella, Piretti and coworkers (13,14).

METHYL LINOLEATE

Unlike methyl oleate, methyl linoleate possesses one activated methylene group which is particularly susceptible to hydrogen atom abstraction. Removal of a hydrogen atom from the activated methylene unit, which is located between the two unconjugated double bonds of the molecule, yields a free radical (III) which is resonance stabilized over five carbon atoms. The attack on methyl linoleate by oxygen may conceivably occur at any one of three sites, as illustrated. Furthermore, each of the three possible positional hydroperoxide isomers (IVa-IVc) has four potential geometric isomers. However, results from early work by Privett, et al. (15) and Cannon, et al. (16) indicated that the hydroperoxides initially formed during autoxidation of methyl linoleate were predominately conjugated dienes possessing cis-trans configurations. Those compounds were apparently capable of undergoing rearrangements to the conjugated



trans-trans isomers. At most, only very small quantities of the unconjugated hydroperoxide (IVb) were formed, although Khan, et al. (17) obtained indirect evidence which suggested that the latter isomer was also produced to some extent. More recently, Chan and Levett (18) detected only four hydroperoxides after autoxidation of methyl linoleate. They were the cis-trans and trans-trans isomers of the conjugated hydroperoxides IVa and IVc. In the cis-trans isomers the trans double bonds were located adjacent to the hydroperoxy groups. Schauenstein (19) investigated the autoxidation of methyl linoleate in dilute aqueous suspensions. Even when the fatty acid esters were dispersed in water the classical mechanism of autoxidation was apparently valid. The same hydroperoxides formed during conventional autoxidations were detected in the aqueous system.

PROOXIDANTS, ANTIOXIDANTS AND SYNERGISTS

Autoxidation is autocatalytic; the hydroperoxide primary products readily cleave to radical fragments which may initiate or propagate the chain reaction. Hydroperoxides may decompose either unimolecularly or bimolecularly, as shown by Equations (7) and (8).

$$ROOH \longrightarrow RO\cdot + HO\cdot \quad (7)$$

$$2ROOH \longrightarrow ROO\cdot + RO\cdot + H_2O \quad (8)$$

High hydroperoxide concentrations coupled with low temperatures favor the latter reaction, while high temperatures promote the unimolecular pathway (7).

Substances which increase the rate of autoxidation are termed prooxidants. Most prooxidants catalyze the decomposition of hydroperoxides and peroxides to free radicals capable of initiating or propagating the autoxidation reaction. Conversely, substances which inhibit autoxidation are termed antioxidants. Most antioxidants react with radicals and transform them to "inert" nonradical products, while others directly decompose hydroperoxides or peroxides to nonradical species. Compounds which enhance the effect of other antioxidants are called synergists; such substances may or may not possess antioxidant properties of their own. Prooxidation, antioxidation and synergism are all discussed in reviews by Ingold (20,21).

PROOXIDANTS

Autoxidation catalysis by transition metal ions is a well known example of prooxidation. The important reactions catalyzed by metal ions are shown by Equations (9) and (10).

$$M^{n+} + ROOH \longrightarrow M^{(n+1)+} + RO\cdot + HO^{-} \quad (9)$$

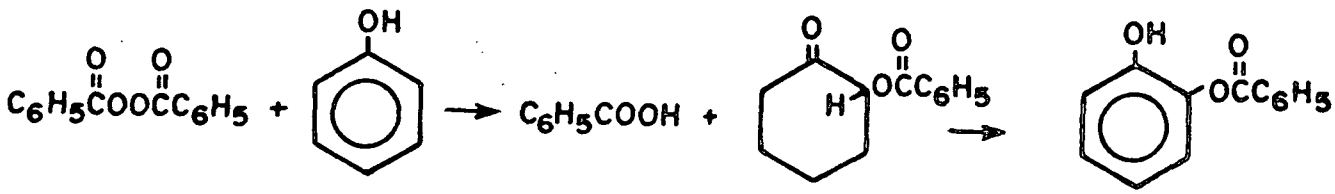
$$M^{(n+1)+} + ROOH \longrightarrow M^{n+} + ROO\cdot + H^{+} \quad (10)$$

One reaction (9) corresponds to oxidation of a hydroperoxide to an alkoxy radical (RO•), while the other (10) represents reduction of a hydroperoxide to a peroxy radical (ROO•). Some metals promote both reactions and are true catalysts. In such cases the net reaction is the same as that represented by Equation (8).

Any other species which can promote the homolytic decomposition of hydroperoxides is a potential prooxidant. Free fatty acids undergo autoxidation more rapidly than fatty acid esters, presumably because the carboxyl groups complex with the hydroperoxides and catalyze their decomposition to free radicals (8,22). In the limiting case, catalytic influences of prooxidants are so effective that the rate of hydroperoxide decomposition approaches, or even attains, the rate of hydroperoxide production, and the autoxidation reaction loses its chain character. The maximum rate of autoxidation, limited only by the rates of Reactions (3) and (6), should then show a second order dependence on fatty acid ester concentration (7).

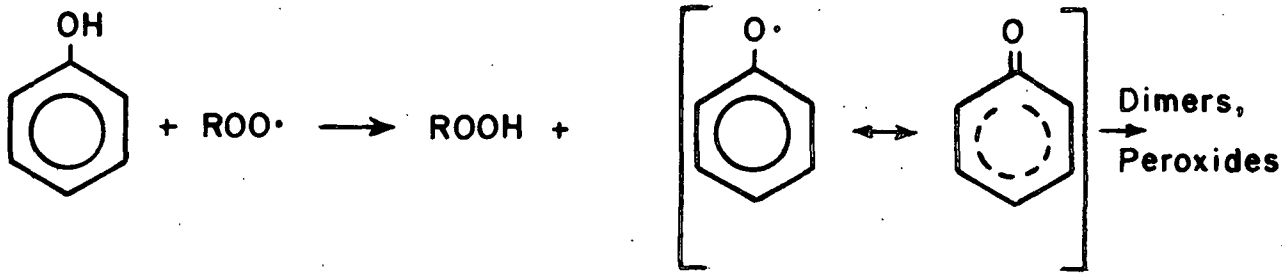
ANTIOXIDANTS

Among the most common antioxidants are phenolic compounds. In some instances phenols may convert peroxides directly to nonradical products. Denney and Denney (23) showed that phenol undergoes a reaction with benzoyl peroxide yielding benzoic acid and catechol monobenzoate, as shown below:



Similar reactions involving hydroperoxides were postulated by Ingold (20).

Phenols may also react with the radical decomposition products of peroxides and hydroperoxides, converting them to products which will not participate in autoxidation. The phenoxy radicals which are created tend to couple with other radicals rather than initiate autoxidation:



SYNERGISTS

The exact mechanism of synergism is not clear, but several possible effects of synergists have been considered (20). They may decompose or deactivate the hydroperoxides formed during reactions between radicals and antioxidants, or they may counteract the prooxidant tendencies of some antioxidants. For example, citric acid, a synergist, suppresses the hydroperoxide decompositions by phenolic antioxidants which would otherwise result in free radical formation.

AUTOXIDATION IN ALKALINE MEDIA

Autoxidation in alkaline media has also been the subject of extensive investigation. Much of the research in this area has been covered in reviews by Russell, et al. (24,25) and Sosnovsky and Zaret (26). All compounds which form carbanions are susceptible to autoxidation in basic systems. These include many hydrocarbons, aldehydes, ketones, esters and anhydrides. The mechanism

of base catalyzed autoxidation, which is summarized by Equations (11) through (20), is similar to that previously described for normal olefin autoxidation.

Ionization	$RH + B^- \longrightarrow R^- + BH$		(11)
Initiation	$R^- + O_2 \longrightarrow R\cdot + O_2\cdot^-$		(12)
	$R^- + O_2\cdot^- \longrightarrow R\cdot + O_2^{-2}$		(13)
	$R^- + A \longrightarrow R\cdot + A\cdot^-$		(14)
Propagation	$R\cdot + O_2 \longrightarrow ROO\cdot$		(15)
	$ROO\cdot + R^- \longrightarrow ROO^- + R\cdot$		(16)
	$A\cdot^- + O_2 \longrightarrow A + O_2\cdot^-$		(17)
Termination	$R\cdot + O_2\cdot^- \longrightarrow ROO^-$		(18)
	$ROO\cdot + O_2\cdot^- \longrightarrow ROO^- + O_2$		(19)
	$2ROO\cdot \longrightarrow$ "Inert" Products		(20)

The initial step of autoxidation in basic media is formation of a carbanion (R^-). For very weakly acidic compounds this may be the rate limiting step. The carbanion then loses one electron in a reaction with oxygen which yields a free radical and superoxide ($O_2\cdot^-$) as shown in Equation (12). The carbanion may also donate one electron to a suitable electron accepting catalyst (A) as shown in Equation (14). The radical formed by Reactions (12)-(14) next combines with molecular oxygen, forming a peroxy radical. The latter reaction (15) is also one of the chain propagating steps in normal autoxidation. The peroxy radical undergoes reaction with a second carbanion in another chain propagating step, which yields another free radical and a peroxy anion. The latter reaction is represented by Equation (16). Reactions (15) and (16) are thus analogous to Reactions (2) and (3) of the classical autoxidation mechanism. The peroxy anion is the primary product of autoxidation in alkaline media. The credibility

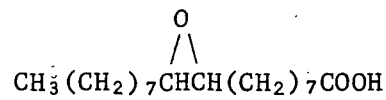
of Reaction (13) is questionable, since Sawyer, et al. (27) recently presented evidence showing that superoxide is a very weak oxidizing agent.

OXIDATION BY SPECIES OTHER THAN MOLECULAR OXYGEN

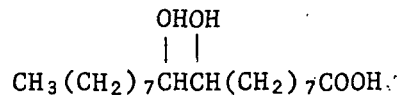
In the presence of a reactive substance such as wood a number of intermediate species, including hydrogen peroxide, hydroperoxides, peroxides and various free radicals, may be formed in significant quantities during the course of autoxidation. All of these compounds may directly or indirectly catalyze fatty acid autoxidation, and in some instances they may react directly with fatty acid molecules.

Evolution of hydrogen peroxide during the alkaline autoxidation of carbohydrates was demonstrated by McCloskey, et al. (28). Hydrogen peroxide formation was observed in similar reactions involving lignin model compounds (29), and it also occurred during the autoxidation of methyl linoleate in water (19). Hydrogen peroxide decomposes thermally or catalytically to hydroxyl and hydroperoxy radicals; these in turn may act as autoxidation initiators, or they may interact directly with double bonds. Formation of peroxyacids is a potential reaction of hydrogen peroxide which could be significant at low pH. Peroxyacids readily react with olefins to form epoxides.

The catalysis of autoxidation by free radicals derived from hydrogen peroxides, hydroperoxides and peroxides has been described. In addition, such species may themselves oxidize unsaturated fatty acids without the participation of molecular oxygen. Swift and Dollear (30) allowed methyl oleate hydroperoxide to react with oleic acid under nitrogen at 90°C. The oleic acid was oxidized to 9,10-epoxystearic acid (V) and 9,10-dihydroxystearic acid (VI) by the hydroperoxide. Expoxides and polyperoxides were among the products of

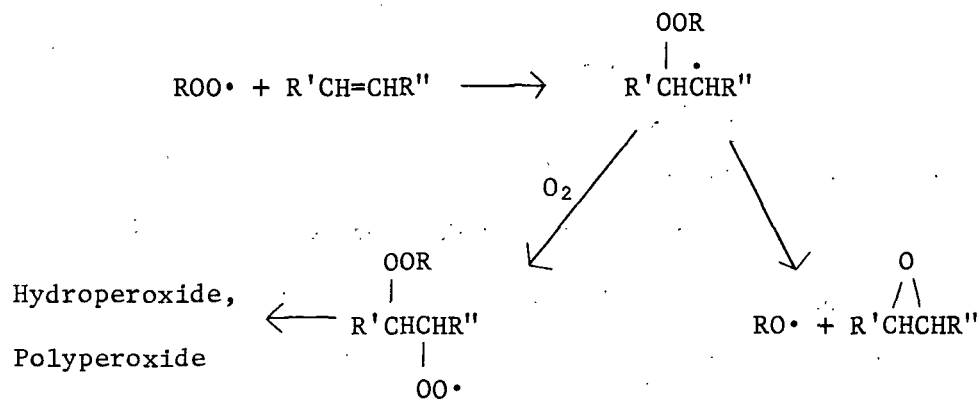


V



VI

reactions between olefins and peroxy radicals discussed by Brill (31) and Ingold (32), while Sheng and Zajacek (33) obtained high yields of epoxides from reactions between hydroperoxides and olefins in the presence of metal catalysts. The probable mechanism of olefin oxidation by hydroperoxides is shown below (32):



The peroxy radical (ROO•) is formed from the hydroperoxide by Equation (8) or catalytically by Equation (10). Oxidations by hydrogen peroxide and peroxides occur by analogous mechanisms.

OTHER POSSIBLE AUTOXIDATION MECHANISMS

The radical chain mechanism of autoxidation, while almost universally accepted, may not be the only reaction pathway applicable to fatty acid autoxidation. The possibility of a chain-initiating step which involved direct reaction between oxygen and double bonds was discussed by Swern, et al. (10). However, the exact nature of the initial reaction, which would become less significant as the radical chain reaction propagated, was not clarified. Rawls (34) suggested that singlet state oxygen might be indirectly responsible for autoxidation initiation, since that species combined directly with double

bonds to form hydroperoxides. Using polarographic techniques, Swern, et al. (35) and Saunders, et al. (36) found evidence which indicated that not all of the peroxidic products of methyl oleate autoxidation were hydroperoxides. Atherton and Hilditch (37) compared autoxidation of methyl oleate at 20 and 120°C. All four of the hydroperoxides (IIa-IId) predicted by the radical chain mechanism were detected at the lower temperature. When the temperature was increased oxidation appeared to occur predominately at the double bond, suggesting a direct interaction between oxygen and the olefin.

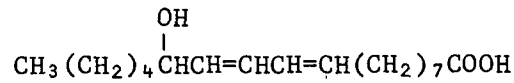
SECONDARY AUTOXIDATION PRODUCTS

Decomposition of hydroperoxides, which are the primary products of fatty acid autoxidation, results in the formation of numerous secondary products, many of which have been identified. The formation of these products was discussed in the review by Swern, et al. (9). The secondary autoxidation products may be divided into three classes. The first class comprises those compounds which are direct derivatives of the parent fatty acid molecule. These include epoxy, keto and hydroxy acids or esters. Another type of compound is formed by scission of carbon-carbon bonds; unsaturated fatty acids are usually cleaved preferentially at or near the locations of their original double bonds. Cleavage products may be acids, alcohols, carbonyl compounds, peroxides or hydrocarbons. The final class consists of polymeric compounds, the structures of which still have not been ascertained.

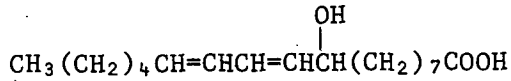
EPOXY, KETO AND HYDROXY ACIDS

Inter- or intramolecular decompositions of hydroperoxides without cleavage of carbon-carbon bonds yield hydroxy, epoxy and keto acids or esters. Hydroperoxides decompose thermally to alkoxy radicals; such reactions are catalyzed by transition metal ions as shown in Equation (9). The alkoxy radicals may

add hydrogen to form hydroxy compounds. Mixtures of hydroxy acids were found among the autoxidation products of various saturated fatty acids by Franzke, et al. (38), while King (39) detected monounsaturated hydroxy esters among the autoxidation products of methyl oleate. Gardner (40) examined secondary products obtained after the ferrous ion catalyzed decomposition of linoleic acid hydroperoxides. Two monohydroxy compounds (VIIa,VIIb) were identified.

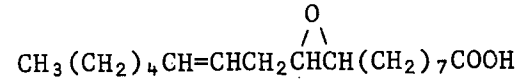


VIIa

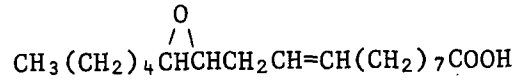


VIIb

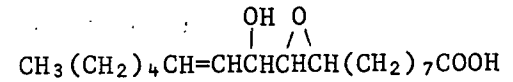
Epoxides, particularly 9,10-epoxystearic acid (V) are commonly detected among the oxidation products of oleic acid and its esters (39,41-43). After autoxidation of linoleic acid, Wu, et al. (44) reported the identification of two epoxy acids (VIIIa,VIIIb) and two epoxy-hydroxy acids (IXa,IXb), while Gardner (40) identified the two latter compounds and two epoxy-keto acids (Xa,Xb).



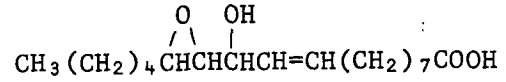
VIIIa



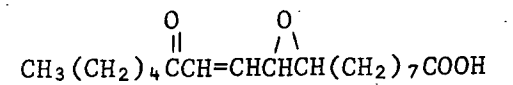
VIIIb



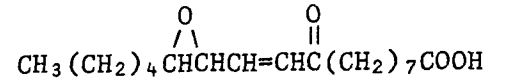
IXa



IXb



Xa

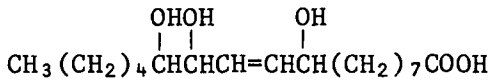


Xb

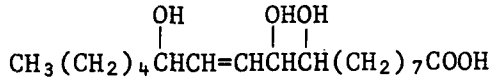
Epoxides formed during reactions between peroxy radicals and unsaturated fatty acids (30) are not true secondary autoxidation products, since they are

not derived from compounds formed directly by reaction with molecular oxygen. However, epoxides may also be created by intramolecular decompositions of hydroperoxides, which are primary products of autoxidation (9,43,44).

Another compound often isolated from the secondary autoxidation products of oleic acid is 9,10-dihydroxystearic acid (VI), which results from hydrolysis of 9,10-epoxystearic acid (37,39,42,45-47). Similarly, two trans unsaturated trihydroxy octadecenoic acids (XIa,XIb) were found among the products of autoxidized linoleic acid by Gardner (40) and Terao and Matsushita (48).



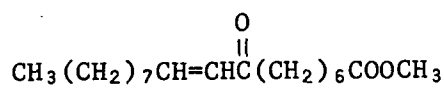
XIa



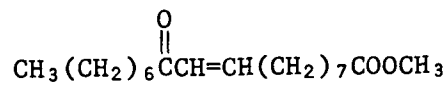
XIb

A monounsaturated dihydroxy acid was also tentatively identified after autoxidation of linoleic acid (48).

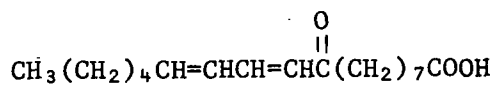
Ketols and α,β-unsaturated carbonyl compounds are other secondary products of autoxidized fatty acids (9). Individual compounds of those types are seldom isolated, but Ellis (49) and King (39) both reported the identification of two α,β-unsaturated keto esters (XIIa,XIIb) among the autoxidation products of methyl oleate. Two analogous compounds (XIIIa,XIIIb) obtained after autoxidation of linoleic acid were identified by Gardner (40).



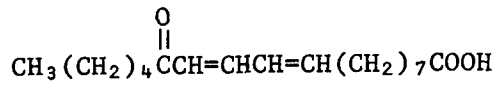
XIIa



XIIb



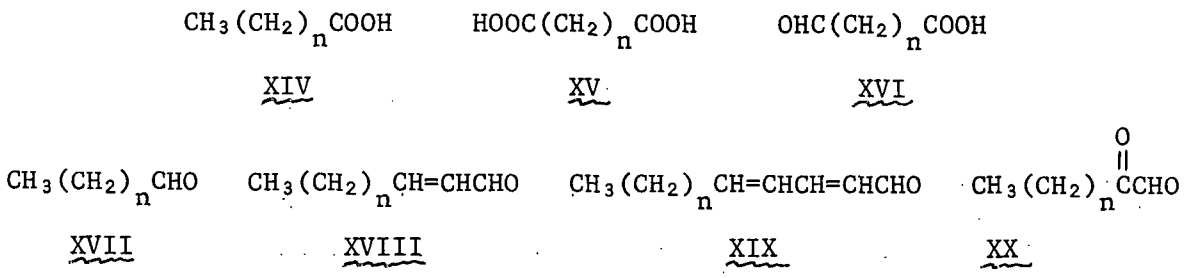
XIIIa



XIIIb

CLEAVAGE PRODUCTS

Cleavage products which have been identified after autoxidation of fatty acids include saturated straight chain carboxylic acids (XIV), dicarboxylic acids (XV) and a variety of alcohols, aldehydes and ketones.



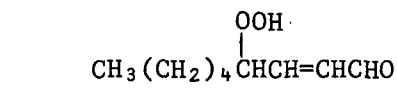
$CH_3(CH_2)_nCOOH$ (XIV) $\quad HOOC(CH_2)_nCOOH$ (XV) $\quad OHC(CH_2)_nCOOH$ (XVI)

$CH_3(CH_2)_nCHO$ (XVII) $\quad CH_3(CH_2)_nCH{=}CHCHO$ (XVIII) $\quad CH_3(CH_2)_nCH{=}CHCH{=}CHCHO$ (XIX) $\quad CH_3(CH_2)_nC(=O)CHO$ (XX)

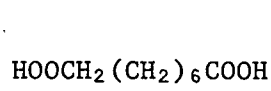
Very complex product mixtures were recovered after autoxidation of saturated fatty acids (38). The predominate cleavage products obtained from autoxidation of oleic acid and its esters (37,39,41,42,45-47,49) were nonanoic acid (XIV, n=7), octanoic acid (XIV, n=6), nonanedioic acid (XV, n=7) and octanedioic acid (XV, n=6). Similarly, hexanoic acid (XIV, n=4) and nonanedioic acid were the major cleavage products of autoxidized linoleic acid identified in one investigation (47), while dicarboxylic acids possessing seven, eight and nine carbon atoms were found after autoxidation of methyl linoleate in water (19).

An aldehyde acid (XVI) was tentatively identified by Ellis (49) after autoxidation of oleic acid, and aldehyde acids were found among the autoxidation products of methyl linoleate by Schoellner and Herzschuh (50). A number of aldehyde acids were detected among the decomposition products of heated cooking oil by Yasuda, et al. (51). Various saturated (XVII) and unsaturated (XVIII, XIX) aldehydes were fatty acid hydroperoxide decomposition products identified by Kimoto and Gaddis (52). Swift, et al. (53) isolated 2-undecenal (XVIII, n=7), an α,β-unsaturated aldehyde, after heating methyl oleate hydroperoxide. Cobb and Day (54) identified several α-keto aldehydes (XX) possessing up to eight carbon atoms after autoxidation of methyl linoleate.

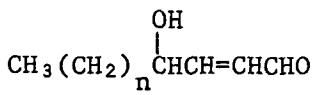
The identification of several unique cleavage products after autoxidation of methyl linoleate in water was reported by Schauenstein (19). Included were two hydroperoxides, 4-hydroperoxy-2-nonenal (XXI) and the methyl ester of 8-hydroperoxyoctanoic acid (XXII). Analogous hydroxy compounds, 4-hydroxy-2-nonenal



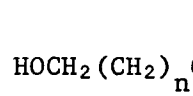
XXI



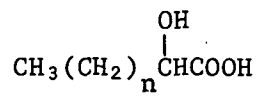
XXII



XXIII



XXIV



XXV

(XXIII, n=4) and the methyl ester of 8-hydroxyoctanoic acid (XXIV, n=6) were also found. Identification of 4-hydroxy-2-octenal (XXIII, n=3) was reported by Esterbauer, et al. (55), who also isolated 2-hydroxyheptanoic acid (XXV, n=4).

The development of combined gas chromatography-mass spectrometry has encouraged numerous investigations into the nature of the secondary autoxidation products obtained from edible fats and oils during deep fat frying. Saturated and unsaturated hydrocarbons, aldehydes, ketones and alcohols were all detected among the volatile oxidation products (56-58). The acidic autoxidation products also comprised very complex mixtures consisting of saturated and unsaturated carboxylic acids, dicarboxylic acids, keto acid, aldehyde acids and hydroxy acids (51,58,59).

POLYMERIC FATTY ACID AUTOXIDATION PRODUCTS

While many of the hydroperoxides and hydroperoxide decomposition products formed during fatty acid autoxidation have been identified, only limited success has been realized in attempts to characterize the polymeric products created

during such reactions. Swern, et al. (46) provided evidence which suggested the existence of ether bonds in the polymers, but formation of carbon-carbon bonds and peroxide linkages has also been postulated (9).

RESULTS AND DISCUSSION

The reactions of molecular oxygen with neat fats and oils under mild conditions have been extensively investigated. However, little attention has been paid to the autoxidation of fatty acids or fatty acid derivatives in aqueous systems, and even less interest has been expressed in their reactions with oxygen and alkali. The present investigation focused upon the reactions of fatty acid soaps and fatty acid methyl esters with oxygen in systems containing aqueous alkali. The magnitudes of temperatures and oxygen pressure exceeded those normally associated with autoxidation, but represented conditions which might be encountered during oxygen-alkali delignification of wood or pulp.

Preliminary reactions were carried out to facilitate identification of the oxidation products formed during reactions of the fatty acid derivatives with oxygen and aqueous alkali. The relative reactivities of individual compounds were also compared in the preliminary study. A half factorial experimental design was subsequently developed, in which the effects of selected variables on the degradation of fatty acid esters were more thoroughly investigated. The results of the factorial design were first interpreted from a perspective which considered only potential yields of tall oil fatty acids. Yields of unreacted fatty acid esters and free fatty acids were measured independently in all reactions. The free acids were derived from esters which underwent saponification, but not oxidation, during the course of reaction. Yields of the major acidic oxidation products were also measured for all reactions associated with the half factorial design. The effects of variations in reaction conditions on the distribution of reaction products were discussed, and reaction mechanisms accounting for formation of the observed products were postulated.

OXIDATIONS OF FATTY ACID SOAP SOLUTIONS

During the preliminary stages of the experimental program alkaline solutions of fatty acid soaps were oxidized in a stirred, Teflon-lined reactor. Fatty acids were first dissolved in 0.3N sodium hydroxide. The soap solutions were then heated to 120°C and pressurized with oxygen to 970 kPa (6.9 kPa = 1.0 psi). During one of the reactions a fatty acid mixture containing 910 mg oleic acid and 35 mg linoleic acid underwent oxidation for 8 hr, while a mixture containing 95 mg oleic acid, 1190 mg linoleic acid and 113 mg linolenic acid was oxidized for 12 hr in a second reaction. Fatty acids in the starting materials

$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ — Oleic Acid

$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$ — Linoleic Acid

$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$ — Linolenic Acid

and reaction products were analyzed by gas-liquid chromatography as their methyl esters. The results of the analyses are presented in Table I.

TABLE I

OXIDATIONS OF AQUEOUS ALKALINE SOAP SOLUTIONS[a]

Reaction No.	Time, hr	Weights of Fatty Acids, mg						Percent Yields		
		Oleic		Linoleic		Linolenic				
		Initial	Final	Initial	Final	Initial	Final	Oleic	Linoleic	Linolenic
1	8	910	740	35	2	--	--	81	6	--
2	12	95	80	1190	162	113	0	84	14	0

[a]Oxidations conducted in 200 mL 0.3N NaOH at 120°C under 690 kPa O_2 pressure.

The reactivities of the fatty acids increased with increasing degrees of unsaturation, as was expected (8-10). The monounsaturated compound, oleic acid, was oxidized to a lesser extent than linoleic acid, which possessed two double bonds separated by an "activated" methylene group. Linolenic acid (cis,cis,cis-9,12,15-octadecatrienoic acid) was present in the starting material used in Reaction (2). This acid, which contained three methylene interrupted double bonds, was completely consumed.

OXIDATIONS OF FATTY ACID METHYL ESTERS

A series of oxidations was next carried out in which fatty acid methyl esters were the starting materials. Two unsaturated esters, methyl oleate and methyl linoleate, were investigated separately in several reactions, while one oxidation was carried out using a pure saturated ester, methyl palmitate. Two identical mixtures containing four saturated esters were oxidized in another pair of reactions. Those compounds, methyl palmitate, methyl stearate, methyl eicosanoate and methyl docosanoate, were derived from straight chain saturated fatty acids containing from sixteen to twenty-two carbon atoms.

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOCH_3$
Methyl Oleate	Methyl Linoleate
$CH_3(CH_2)_{14}COOCH_3$	$CH_3(CH_2)_{16}COOCH_3$
Methyl Palmitate	Methyl Stearate
$CH_3(CH_2)_{18}COOCH_3$	$CH_3(CH_2)_{20}COOCH_3$
Methyl Eicosanoate	Methyl Docosanoate

All the methyl esters were oxidized in the presence of a substrate, either cotton linters or preextracted wood meal. Prior to each reaction, the substrate was impregnated with a pure ester or mixture of esters. The impregnated substrate was mixed thoroughly with an aqueous solution of alkali, either sodium hydroxide, sodium carbonate or sodium bicarbonate. The volume of water was adjusted to effect complete absorption of the alkali solution by the substrate. The reactants thus comprised a porous mass of high surface area, allowing intimate contact with the gaseous oxygen. The oxidations were carried out in a 1 liter modified Parr bomb which was not stirred or agitated. The conditions for this series of reactions are listed in Table II, while the yields of unoxidized starting materials are reported in Table III. Fatty acids recovered as unchanged esters are differentiated from those which were saponified and recovered as free acids.

TABLE II

OXIDATIONS OF FATTY ACID METHYL ESTERS: REACTION CONDITIONS

Reaction No.	Substrate	Temp., °C	Time, hr	Pressure O_2, kPa	Alkali
3	50 g Wood meal	140	4	970	11 g NaOH
4	50 g Wood meal	140	4	970	11 g NaOH
5	50 g Wood meal	140	4	970	11 g NaOH
6	50 g Wood meal	140	4	970	14.6 g Na_2CO_3
7	30 g Cotton linters	130	5	2100	11 g NaOH
8	30 g Cotton linters	130	5	2100	23.1 g $NaHCO_3$
9	30 g Cotton linters	130	5	2100	11 g NaOH
10	30 g Cotton linters	130	5	2100	11 g NaOH

As was observed during the oxidations of fatty acid soap solutions, the reactivities of the fatty acid methyl esters increased with the extent of unsaturation. The results from Reactions (3)-(5), which were carried out under identical conditions using three different fatty acid esters, showed that methyl

linoleate was oxidized to a greater extent than methyl oleate, while methyl palmitate was by far the most stable compound.

TABLE III

OXIDATIONS OF FATTY ACID METHYL ESTERS: FATTY ACID YIELDS

Reaction No.	Starting Material and Weight of Methyl Ester, g		Unoxidized Starting Material Weights as Methyl Esters, g			Total Yield, %
			Esters	Acids	Total	
3	Methyl palmitate	5.00	N.D.	N.D.	4.47	89
4	Methyl oleate	5.00	N.D.	N.D.	2.46	49
5	Methyl linoleate	5.00	0.07	1.58	1.65	33
6	Methyl linoleate	5.00	1.25	0.16	1.41	28
7	Methyl palmitate	1.11	0	1.04	1.04	94
	Methyl stearate	0.77	0	0.71	0.71	92
	Methyl eicosanoate	0.45	0	0.40	0.40	89
	Methyl docosanoate	0.52	0	0.49	0.49	94
8	Methyl palmitate	1.11	0.98	0.01	0.99	89
	Methyl stearate	0.77	0.70	0.01	0.71	92
	Methyl eicosanoate	0.45	0.40	0	0.40	89
	Methyl docosanoate	0.52	0.46	0	0.46	88
9	Methyl oleate	4.00	0	3.53	3.53	88
10	Methyl linoleate	4.00	0	2.40	2.40	60

Particularly noteworthy among the results presented in Table III is the effect of alkali upon saponification of the fatty acid methyl esters. Equivalent weights of methyl linoleate were oxidized in Reactions (5) and (6), and the reaction conditions differed only in the nature of the alkali. The extents of linoleate degradation were nearly the same in both reactions. However, the unoxidized starting material was almost completely saponified by sodium hydroxide, but it was saponified only to a limited extent when the hydroxide was replaced with carbonate. Similarly, Reactions (7) and (8) were carried out in systems which contained either sodium hydroxide or sodium bicarbonate, but which were otherwise identical. The yields of starting material approached or exceeded 90% after both reactions. Sodium hydroxide effected complete saponification of the esters, while almost no saponification occurred in the system charged with bicarbonate.

While the results of Reactions (1)-(10) provided other insights into the behavior of fatty acids and fatty acid esters during reactions with oxygen and alkali, identification of reaction products was the primary objective of those preliminary oxidations. Product analyses were attempted after each reaction. Although no oxidation products of saturated fatty acids were detected, a large number of compounds were eventually identified after oxidations of the unsaturated fatty acids and esters. The results of the product analyses are discussed in later sections.

DEVELOPMENT OF THE HALF FACTORIAL EXPERIMENTAL DESIGN

After the preliminary reactions had been completed, a half factorial experimental design was developed to investigate the effects of major reaction variables on the degradation of tall oil fatty acid esters by oxygen and alkali. This program was implemented and interpreted according to procedures described by Davies (60).

VARIABLES AND COMPOUNDS INVESTIGATED

The effects of five variables on the reactions of two fatty acid methyl esters, methyl oleate and methyl linoleate, were investigated. The five variables incorporated into the experimental design were defined as temperature, reaction time, oxygen pressure, alkali, and substrate. Each variable was assigned two levels, a high value and a low value, representing the extreme conditions likely to be encountered during oxygen-alkali delignification. The temperatures were 100 and 160°C, the reaction times were 2 and 8 hr, and the oxygen pressures were 690 and 3500 kPa. The high and low levels of alkali were defined as sodium bicarbonate and sodium hydroxide, respectively, based on the assumption that more extensive fatty acid oxidation would occur in a system containing the weaker base. Because an antioxidant effect associated

with lignin was expected, cotton linters and wood meal were chosen as the high and low levels, respectively, of the substrate variable.

The absolute quantities of sodium hydroxide, sodium bicarbonate, wood meal and cotton linters employed in all reactions constituting the half factorial design are shown in Table IV. Also enumerated in the table are the high and low magnitudes of the other three variables. In all reactions associated with the half factorial design, each variable was held at one of the two levels shown. To satisfy the complete design, each variable was maintained at its higher level in exactly one-half of all reactions, and at its lower level in the remainder.

TABLE IV

VARIABLES INCORPORATED INTO THE HALF FACTORIAL DESIGN

Variable	Low Level	High Level
Temperature	100°C	160°C
Reaction time	2 hours	8 hours
Oxygen pressure	690 kiloPascals	3500 kiloPascals
Alkali	11 g NaOH	23.1 g $NaHCO_3$
Substrate	50 g wood meal	30 g cotton linters

Temperature

Temperature was included among the variables investigated to determine whether high or low magnitudes might be more conducive to recovery of tall oil fatty acids. Comparison of the influence of temperature with the effects of other variables could aid determination of reaction conditions compatible with both delignification and tall oil fatty acid recovery. The temperature limits chosen represented the probable extremes of any potential oxygen-alkali delignification process. The reaction between oxygen and wood is very slow below

100°C, while high temperatures promote excessive degradation of cellulose. All reactions were initiated at the same temperature, 80°C. The rise to the assigned temperature level was effected using a constant temperature oil bath, and it was further promoted by the exothermic reaction between oxygen and the substrate.

Reaction Time

The effect of reaction time on oxidation of the fatty acid esters was also examined to permit its direct comparison with the effect of other variables. The lower level chosen for this variable was 2 hr. Usually no more than one hour was required for the reaction systems to attain thermal equilibrium.

Oxygen Pressure

The influence of oxygen pressure on the degradation of fatty acids is not as straightforward as the effects of either temperature or reaction time. During normal fatty acid autoxidation, little increase in the rate of reaction is observed when the oxygen pressure is increased beyond a critical magnitude, which depends on the nature of the reactant, and which may have an absolute value as low as 25 kPa (6,7). Oxygen pressure remains a significant variable only if chain propagating free radicals are created at a rate which exceeds the rate of reaction between those short-lived radicals and oxygen. At high pressures reactions of the radicals with oxygen are much more rapid than chain initiating or chain terminating reactions, and no increase in the overall rate of autoxidation is achieved when the pressure is raised further. Oxygen pressure was included among the variables examined in this investigation to determine if a similar situation would exist in the complex, heterogeneous system encountered during delignification. The low level of this variable was far above the expected rate-limiting critical value associated with normal autoxidation and lower than the magnitudes usually employed in oxygen-alkali delignification.

The high level of oxygen pressure was limited by the structural capabilities of the reaction vessel.

Alkali

The high and low levels of alkali were defined as sodium bicarbonate and sodium hydroxide, respectively. Equimolar amounts of each base were employed in all reactions. Bicarbonate was chosen as the higher level of this variable on the basis of previous work by Pearl and Dickey (61), who found that tall oil losses during oxygen-alkali delignification increased if hydroxide was replaced with carbonate or bicarbonate.

Substrate

Pearl and Dickey (61) also observed a "protective effect" related to wood when tall oil fatty acids underwent reaction with oxygen and alkali; the presence of wood in the reaction system retarded degradation of the fatty acids. To further investigate the protective effect of wood on fatty acid oxidation, a fifth variable, defined as substrate, was included in the experimental program. Lignin-free cotton linters were chosen as the higher level of this variable, while preextracted loblolly pinewood meal was defined as its lower level.

Fatty Acid Esters

Methyl oleate, a monounsaturated ester, and methyl linoleate, which possesses two double bonds, were the fatty acid derivatives chosen as starting materials for this investigation. Oleic acid and linoleic acid are by far the two most important tall oil fatty acids (5), both in terms of abundance and value. Saturated fatty acids are also important tall oil components, but the preliminary reactions (Table III) had shown that such compounds were very resistant to reaction with oxygen and alkali. Therefore, to simplify the system,

only reactions of the two unsaturated compounds were investigated. Although the fatty acids in wood exist primarily as triglycerides, methyl esters were utilized because of the relative ease with which they could be obtained. The quantities of esters employed, 1.72 g methyl oleate and 2.12 g methyl linoleate, were about eight times the amounts which occur naturally in wood. Because the methyl oleate starting material contained some impurities, 0.16 g of unidentified fatty acids or esters were also present in each reaction.

Reaction System

All of the reactions comprising the final half factorial experimental plan were designed to represent a high consistency oxygen-alkali delignification process. Prior to each reaction, the fatty acid esters were dissolved in acetone and slurried with substrate (50 g wood meal or 30 g cotton linters). The acetone was removed by evaporation under reduced pressure, leaving the substrate impregnated with the fatty acid methyl esters.

To make the system consistent with that employed by Pearl and Dickey (3), the alkali charge in every reaction was 17% (expressed as Na_2O) based on 50 g dry wood. The alkali was dissolved in 180 mL water, and the alkali solutions were completely absorbed by the porous substrates.

FULL FACTORIAL EXPERIMENTAL DESIGN

A full factorial design incorporating all five of the variables listed in Table IV would require thirty-two experiments, and it would include all possible combinations of the five variables at their high and low levels. Each variable would be at its high level in sixteen reactions and at its low level in the other sixteen. Factorial designs allow simultaneous and independent measurements of effects and interactions for several variables in a minimum number of experiments. The overall effect of a variable is defined as its main effect. Interactions

exist if the effect of a variable is dependent on the level of one or more of the other variables. An interaction between two single variables is a two-factor interaction. Interactions among three, four or five variables are three-factor, four-factor or five-factor interactions. A full factorial plan for all five variables would allow measurement of five main effects, ten two-factor interactions, ten three-factor interactions, five four-factor interactions and one five-factor interaction. The effects and interactions together would thus represent thirty-one unique pieces of information derived from thirty-two unique trials.

Main Effects of Variables

The main effect of a variable is the average change in a response, measured over all reactions, which results when the magnitude of the variable is raised from its lower level to its higher level. The response is an arbitrarily chosen measurement taken from each reaction. The main effect of a variable is calculated by determining the average response in all those reactions involving the variable at its lower level, and subtracting that quantity from the average response determined in all reactions involving the variable at its higher level.

Interactions Among Variables

Interactions become important if the effect of a variable depends upon the level of one or more of the other variables. To calculate a two-factor interaction between any two variables, the effects of one variable must be considered independently in the two sets of reactions defined by the high and low levels of the other variable. The effect of the first variable is calculated in those reactions which involve the second variable only at its lower level. That quantity is subtracted from the effect of the first variable which is derived from those reactions involving the second variable only at its higher level. The difference between those two effects, which is divided by two to normalize it on the

same basis as the main effects, defines the two-factor interaction. If the magnitude of a two-factor interaction is significant, then the main effect of either variable may be meaningless unless consideration is given to the level of the other.

A three-factor interaction exists if the two-factor interaction between any two variables is dependent upon the level of a third variable. Higher order interactions, which involve four or more variables, are defined similarly. By definition, all interactions are symmetrical. The interaction between any two variables will always possess the same sign and magnitude, regardless of how the interaction is calculated. In other words, if the effect of one variable depends upon the level of another, then the inverse is also true. Similarly, an interaction among any group of three or more variables may be considered as the interaction of any one of them with the combined interaction of the others.

FRACTIONAL FACTORIAL DESIGNS

While all effects and interactions may be determined unambiguously in a full factorial design, the magnitudes of higher order interactions are often negligibly small in comparison with the main effects and lower order interactions. Because of this, fractional factorial designs may be devised in which the effects and lower order interactions of certain variables are confounded with the higher order interactions of other variables. Confounding occurs when the experimental plan is purposely designed such that two or more different effects or interactions are represented by the same calculation. When an effect or interaction is confounded with another interaction which is known to be negligible, then the actual quantity determined represents only the nonnegligible entity. By properly confounding interactions and effects, additional variables may be incorporated into an established factorial plan without increasing the number of experiments necessary to satisfy the plan.

THE HALF FACTORIAL EXPERIMENTAL DESIGN

In the present investigation, a full factorial design for four factors, which required sixteen experiments, was first devised. An additional variable was then added to the plan by confounding the main effect of that fifth variable with the four-factor interaction of the original four variables. Each two-factor interaction between the fifth variable and each of the other four variables was similarly confounded with the three-factor interaction of the remaining three.

The experimental design finally developed corresponds to a half factorial design for five variables, which is a specific example of a fractional factorial design. The half factorial design, outlined in Table V, consists of sixteen experiments. If the levels of all variables in all sixteen of those reactions are reversed, another set of sixteen trials, corresponding to the other half of the full factorial design, is obtained. The design shown in Table V may be derived from a full factorial plan involving any four of the variables. The four-factor interaction of the four variables is always confounded with the main effect of the fifth variable in the half factorial design. For example, the main effect of substrate is confounded with the four-factor interaction among temperature, reaction time, oxygen pressure and alkali. The value calculated for the main effect is actually the sum of those two quantities, but the four-factor interaction is presumed to have a numerical value of zero. Similarly, the two-factor interaction between any two variables of the half factorial design is always confounded with the three-factor interaction among the other three. The two-factor interaction between temperature and oxygen pressure, for example, also includes the three-factor interaction among reaction time, alkali and substrate. However, the latter interaction is assumed to be zero.

TABLE V

HALF FACTORIAL DESIGN FOR OXIDATION OF FATTY ACID METHYL ESTERS[a]

Reaction No.	Temperature, °C	Reaction Time, hr	Pressure O_2, kPa	Alkali	Substrate
1F	100	2	690	NaOH	Cotton
2F	160	2	690	NaOH	Wood
3F	100	8	690	NaOH	Wood
4F	160	8	690	NaOH	Cotton
5F	100	2	3500	NaOH	Wood
6F	160	2	3500	NaOH	Cotton
7F	100	8	3500	NaOH	Cotton
8F	160	8	3500	NaOH	Wood
9F	100	2	690	$NaHCO_3$	Wood
10F	160	2	690	$NaHCO_3$	Cotton
11F	100	8	690	$NaHCO_3$	Cotton
12F	160	8	690	$NaHCO_3$	Wood
13F	100	2	3500	$NaHCO_3$	Cotton
14F	160	2	3500	$NaHCO_3$	Wood
15F	100	8	3500	$NaHCO_3$	Wood
16F	160	8	3500	$NaHCO_3$	Cotton
17F[b]	130	5	2100	NaOH	Wood
18F[b]	130	5	2100	NaOH	Wood
19F[b]	130	5	2100	NaOH	Wood
20F[b]	130	5	2100	$NaHCO_3$	Wood
21F[b]	130	5	2100	$NaHCO_3$	Wood

[a]All reaction systems initially contained 1.72 g methyl oleate and 2.12 g methyl linoleate.

[b]Reactions 17F-21F were not part of the half factorial design, but were included to provide an estimate of experimental error.

On the assumption that all three- and four-factor interactions are negligibly small, the main effects of all five variables, and all ten of their two-factor interactions, may be determined from the sixteen experiments which comprise the half factorial design. However, since there is no replication of experiments, and since all higher-order interactions are already confounded with effects or interactions whose magnitudes may be significant, the design

contains no inherent means of determining experimental error. An estimate of variance may be derived by assuming that certain two-factor interactions are negligible. The magnitudes calculated for those interactions are then assumed to represent experimental error only. However, since an external estimate of error was desired, five additional reactions (17F-21F), representing two sets of replicate trials, were also carried out. The temperature, reaction time and oxygen pressure were averages of the high and low values employed in the actual half factorial design. The magnitudes of those three variables were thus 130°C, 5 hr and 2100 kPa, respectively. In one set of trials the alkali was sodium hydroxide, while sodium bicarbonate was used in the other. All five reactions were run in the presence of wood meal. Originally, only two sets of duplicate reactions (17F-18F and 20F-21F) were envisioned, but Reaction 19F was also included because an excessively large discrepancy was observed between the results of Reactions 17F and 18F.

RECOVERY OF FATTY ACID ESTERS, FREE FATTY ACIDS AND OXIDATION PRODUCTS

The products of Reactions 1F-21F (Table V) were extracted with ether and fractionated on DEAE Sephadex, a weakly basic anion exchange resin, into three fractions as described by Zinkel and Rowe (62). The first fraction contained unchanged fatty acid methyl esters, neutral compounds which were not retained on the ion exchange resin. The second fraction consisted of weakly acidic material which was eluted from the resin with a saturated solution of carbon dioxide in ether-methanol. Included among the weak acids were free fatty acids formed by saponification of the methyl esters. Since the free fatty acids had not undergone oxidation, they were also considered to be unreacted starting material. The more strongly acidic compounds retained on the ion exchanger after elution with carbon dioxide included many of the fatty acid oxidation products.

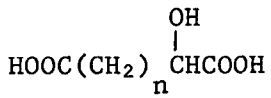
The strong acids were stripped from the resin with alternate washings of 1N hydrochloric acid and 1N potassium hydroxide. The fatty acid methyl esters (neutrals), free fatty acids (weak acids) and fatty acid oxidation products (strong acids) were all analyzed by gas-liquid chromatography. The latter were analyzed as their trimethylsilyl derivatives, while the fatty acids were analyzed as their methyl esters. The analytical procedures employed are described in more detail in Appendix III.

To test the efficiency of the overall analytical scheme, a control experiment was carried out in which oxidized wood meal was impregnated with a mixture of fatty acid methyl esters, free fatty acids and selected fatty acid oxidation products. Before impregnation, the wood meal had been oxidized under the same conditions as were employed in Reactions 17F-19F. The impregnated control mixture was analyzed according to the same procedures used during analysis of each of the actual reaction product mixtures. The results of this analysis are presented in Table VI.

The measured recoveries of oleic acid and linoleic acid were 90%. Eighty-nine percent of the methyl oleate was recovered, while all of the methyl linoleate was accounted for. These results suggest that losses of up to 10% may be expected for the free fatty acids and fatty acid methyl esters. The fatty acids and their esters were effectively separated from each other, and from the more strongly acidic oxidation products.

Among the fatty acid oxidation products, good recoveries of the higher dicarboxylic acids (XV) and α-hydroxy acids (XXV) were achieved. One of the latter compounds, 2-hydroxybutyric acid (XXV, n=1), was recovered in excessively high yield. However, this compound has been detected in kraft black liquor (63), and it may be a product of the reaction between wood and oxygen-alkali. Recoveries

of the oxidation products tended to decrease as their water solubilities increased. α-Hydroxydicarboxylic acids (XXVI) were fatty acid oxidation products identified during this investigation:



XXVI

Although two low molecular weight compounds of this class, malic acid (XXVI, n=1) and 2-hydroxypentanedioic acid (XXVI, n=2), were added to the control mixture, they were not detected among the compounds recovered. Both compounds were very soluble in water, and almost insoluble in ether. 2-Hydroxydecanedioic acid (XXVI, n=7) was also added to the control mixture. This compound, appreciably soluble in ether, was recovered in 87% yield.

TABLE VI

TEST OF THE ANALYTICAL PROCEDURE

Compounds Added to Control Mixture Compound - Structure	Wt., mg	Recovery of Compounds: Neutrals, mg	%	Weak Acids, mg	%	Strong Acids, mg	%
Methyl oleate	586	523	89				
Methyl linoleate	453	460	102				
Oleic acid	660			593	90		
Linoleic acid	542			487	90		
Nonanoic acid - XIV, n=7	76					27	36
Succinic acid - XV, n=2	187					145	78
Hexanedioic acid - XV, n=4	85					75	88
Heptanedioic acid - XV, n=5	141					145	103
Octanedioic acid - XV, n=6	199					198	99
Nonanedioic acid - XV, n=7	330					345	105
2-Hydroxybutyric acid - XXV, n=1	51					75	147
2-Hydroxypentanoic acid - XXV, n=2	162					175	108
2-Hydroxyhexanoic acid - XXV, n=3	170					168	99
Malic acid - XXVI, n=1	46					0	0
2-Hydroxypentanedioic acid - XXVI, n=2	82					0	0
2-Hydroxydecanedioic acid - XXVI, n=7	149					129	87
9,10-Dihydroxystearic acid - VI	259					70	27

Poor recoveries of nonanoic acid (XIV, n=7) and 9,10-dihydroxystearic acid (VI) were realized. Both compounds may have been only intermediately acidic and partially eluted from the ion exchange resin with carbon dioxide.

RESULTS OF THE HALF FACTORIAL EXPERIMENTAL DESIGN

RECOVERIES OF UNOXIDIZED OLEATE AND LINOLEATE

The responses measured from each reaction associated with the half factorial experimental design (Table V) were the percent yields of unoxidized starting materials. Two such yields were determined for all reactions, one each for oleate and linoleate. The recoveries of fatty acid methyl esters (neutrals) and free fatty acids (weak acids) were measured separately and were combined to give the overall yields. The results are presented in Table VII.

MAIN EFFECTS AND INTERACTIONS

Tests of Significance

The main effects and interactions of all variables were calculated from the total percent yields of oleate and linoleate, which were listed in the last two columns of Table VII. The yields of the two compounds were treated independently. The significance of each effect or interaction was tested by an analysis of variance (60,64). Shown in Table VIII are the mean squares of the effects and interactions related to the yield of oleate. The mean squares for the effects and interactions involving the yield of linoleate are presented in Table IX. Those mean squares were tested against error mean square terms derived from the results of Reactions 17F-21F. In each case, the error mean square (EMS) was obtained from the sum of squares about the means of those reactions. That sum of squares contained five terms, three from Reactions 17F-19F and two from Reactions 20F and 21F. The error mean square corresponded to the sum of squares

divided by three degrees of freedom, two from Reactions 17F-19F and one from the other two reactions.

TABLE VII

RECOVERIES OF UNOXIDIZED OLEATE AND LINOLEATE

Reaction No.	Yield of Starting Material[a] g, as Methyl Esters						Total Percent Yield	
	Neutrals		Weak Acids		Total			
	Oleate	Linoleate	Oleate	Linoleate	Oleate	Linoleate	Oleate	Linoleate
1F	0.01	0.01	1.49	1.58	1.50	1.59	87.2	75.0
2F	0.10	0.05	1.28	1.31	1.38	1.36	80.2	64.2
3F	0.08	0.06	1.30	1.43	1.38	1.49	80.2	70.3
4F	0	0	1.39	1.05	1.39	1.05	80.8	49.5
5F	0.28	0.22	0.94	1.05	1.22	1.27	70.9	59.9
6F	0	0	1.27	0.98	1.27	0.98	73.8	46.2
7F	0	0	1.39	1.38	1.39	1.38	80.8	65.6
8F	0.08	0.02	0.46	0.30	0.54	0.32	31.4	15.1
9F	1.37	1.31	0.02	0.02	1.39	1.33	80.8	62.7
10F	0.36	0.28	0.02	0.01	0.38	0.29	22.1	13.7
11F	0.39	0.02	0.02	0.01	0.41	0.03	23.8	1.4
12F	0.77	0.73	0.09	0.10	0.86	0.83	50.0	39.2
13F	1.03	0.20	0.02	0	1.05	0.20	61.0	9.4
14F	0.53	0.84	0.02	0.02	0.55	0.86	32.0	40.6
15F	0.77	0.49	0.02	0.01	0.79	0.50	45.9	23.6
16F	0.16	0.08	0.02	0.02	0.18	0.10	10.5	4.7
17F[b]	0.33	0.16	0.60	0.58	0.93	0.74	54.1	34.9
18F[b]	0.12	0.05	1.06	1.06	1.18	1.11	68.6	52.4
19F[b]	0.29	0.12	0.84	0.93	1.13	1.05	65.7	49.5
20F[b]	0.69	0.64	0.01	0.01	0.70	0.65	40.7	30.7
21F[b]	0.78	0.70	0.01	0.01	0.79	0.71	45.9	33.5

[a] All reaction systems initially contained 1.72 g methyl oleate and 2.12 g methyl linoleate.

[b] Reactions 17F-21F were not part of the half factorial design, but were included to provide an estimate of experimental error.

TABLE VIII

ANALYSIS OF VARIANCE FOR REACTIONS OF METHYL OLEATE

Effect or Interaction	Degrees of Freedom	Sum of Squares = Mean Square	F-Test[a], mean square/EMS
Temperature	1	1402.5	32.09**
Reaction time	1	683.8	15.65**
Oxygen pressure	1	610.1	13.96**
Alkali	1	4199.0	96.09***
Substrate	1	61.6	1.41
Temperature-time	1	71.4	1.63
Temperature-pressure	1	324.0	7.41*
Temperature-alkali	1	121.0	2.77
Temperature-substrate	1	21.6	0.49
Time-pressure	1	70.6	1.62
Time-alkali	1	44.9	1.03
Time-substrate	1	4.2	0.10
Pressure-alkali	1	122.1	2.79
Pressure-substrate	1	948.6	21.71**
Alkali-substrate	1	1428.8	32.70**

Reactions 17F-21F	Degrees of Freedom	Sum of Squares	Mean Square = EMS
Error variance	3	131.2	43.7

[a] With three degrees of freedom, the significance levels of the F-test are 5.54 at the 10% level (*), 10.1 at the 5% level (**), and 34.1 at the 1% level (***).

[b] The error variance was determined from the sum of squares about the means of reactions 17F-19F and 20F-21F.

The significance of each effect and interaction was determined from its variance (mean square) using the F-test (64). An effect or interaction was considered significant if there was less than a 5% probability that its magnitude was due to experimental error. If that probability was less than 1%, then the effect or interaction was considered highly significant. An effect or interaction was still considered probably significant if the F-test was between the 5 and 10% significance levels.

TABLE IX

ANALYSIS OF VARIANCE FOR REACTIONS OF METHYL LINOLEATE

Effect or Interaction	Degrees of Freedom	Sum of Squares = Mean Square	F-Test[a], mean square/EMS
Temperature	1	560.5	9.42*
Reaction time	1	654.1	10.99**
Oxygen pressure	1	768.7	12.92**
Alkali	1	3921.9	65.91***
Substrate	1	757.6	12.73**
Temperature-time	1	6.4	0.11
Temperature-pressure	1	5.2	0.08
Temperature-alkali	1	586.9	9.86*
Temperature-substrate	1	25.3	0.43
Time-pressure	1	4.1	0.07
Time-alkali	1	10.1	0.17
Time-substrate	1	196.7	3.31
Pressure-alkali	1	70.1	1.18
Pressure-substrate	1	435.8	7.32*
Alkali-substrate	1	1674.9	28.15**
Reactions 17F-21F	Degrees of Freedom	Sum of Squares	Mean Square = EMS
Error Variance[b]	3	179.8	59.5

[a] With three degrees of freedom, the significance levels of the F-test are 5.54 at the 10% level (*), 10.1 at the 5% level (**), and 34.1 at the 1% level (***).

[b] The error variance was determined from the sum of squares about the means of reactions 17F-19F and 20F-21F.

Magnitudes and Signs of Effects and Interactions

The numerical values of all main effects and interactions are presented in Table X. The calculation of those effects and interactions is described in Appendix X, which also contains further discussion of the analysis of variance.

As the signs of the main effects listed in Table X indicate, raising any one of the five variables from its low level to its high level increases the extent of fatty acid oxidation. The negative effect of temperature shows that an average 18.7% decrease in the yield of oleate, and an average 11.8% decrease in the yield of linoleate, result if the temperature is increased from 100 to

160°C. Similarly, the negative effects of reaction time and oxygen pressure show that the yields of oleate and linoleate decrease an average of from 12 to 14% if the reaction time is extended from 2 to 8 hr or if the oxygen pressure is raised from 690 to 3500 kPa. The negative sign and large magnitude of the alkali effect show that fatty acid yields decrease by more than 30%, on the average, when hydroxide is replaced with bicarbonate. The negative sign of the substrate effect shows that fatty acid oxidation is more extensive in the presence of cotton than in the presence of wood. The magnitude of the substrate effect is not significant with respect to the yield of oleate. However, substrate interacts significantly with both alkali and oxygen pressure, and the substrate variable is itself considered significant on that basis.

TABLE X

MAIN EFFECTS AND INTERACTIONS OF REACTION VARIABLES

Main Effect or Interaction	Sign and Magnitude[a]	
	Oleate Yield	Linoleate Yield
Temperature	-18.7**	-11.8*
Reaction time	-13.1**	-12.8**
Oxygen pressure	-12.4**	-13.9**
Alkali	-32.4***	-31.3***
Substrate	- 3.9	-13.8**
Temperature-time	+ 4.2	- 1.3
Temperature-pressure	- 9.0*	- 1.1
Temperature-alkali	- 5.5	+12.1*
Temperature-substrate	+ 2.3	+ 2.5
Time-pressure	- 4.2	+ 1.0
Time-alkali	- 3.4	- 1.6
Time-substrate	+ 1.0	+ 7.0
Pressure-alkali	+ 5.5	+ 4.2
Pressure-substrate	+15.4**	+10.4*
Alkali-substrate	-18.9**	-20.5**

[a]Effects or interactions which are considered significant or probably significant are indicated by a double asterisk (**) or a single asterisk (*), respectively, while those which are considered highly significant are denoted by a triple asterisk (***).

To obtain a more complete understanding of the substrate effect, its interactions with the other variables must be considered. Substrate is involved in two significant two-factor interactions. The positive sign of the pressure-substrate interaction shows that the effect of substrate is greater at low pressure than at high pressure. Therefore, more extensive fatty acid oxidation occurs when wood is replaced with cotton at low oxygen pressure; this effect is less pronounced at high pressure. The pressure-substrate interaction may also be interpreted from a perspective which focuses on the effect of pressure. In the presence of wood, increasing the oxygen pressure decreases the fatty acid yields significantly. However, in the presence of cotton, the level of oxygen pressure has little, if any, effect on degradation of the fatty acids.

The negative sign and large magnitude of the alkali-substrate interaction show that alkali has a relatively greater effect at the high level of substrate, which is cotton linters. In the presence of cotton, replacing hydroxide with bicarbonate should result in greatly reduced fatty acid yields. A similar effect, but of much lesser magnitude, should be observed in the presence of wood meal. With respect to the yields of both oleate and linoleate, the alkali-substrate interaction has a greater magnitude than the substrate effect itself. In the presence of bicarbonate, decreased fatty acid yields should result when the substrate is changed from its lower level, wood meal, to its higher level, cotton linters. However, the large magnitude of the alkali-substrate interaction suggests that the effect of substrate will be reversed in the presence of hydroxide. In that system, fatty acid yields should increase when wood meal is replaced with cotton linters.

Only two other significant interactions were observed. One of them, a temperature-pressure interaction, was significant only when related to the yield of oleate. The interaction possessed a negative sign, indicating that the effect

of either one of the variables, temperature or pressure, was greater at the higher level of the other. The other interaction was a temperature-alkali interaction, and it was significant only with respect to the yield of linoleate. That interaction had a positive sign, indicating that the effect of either one of the variables, temperature or alkali, was more pronounced at the lower level of the other. Neither of these two interactions was significant for the yields of both oleate and linoleate. The interactions may have represented accumulated experimental errors, or they may have resulted from circumstances unique to the reactions of only one of the starting compounds. The two-factor interactions may also have been confounded with three-factor interactions whose magnitudes were large enough to make the combined two- and three-factor interactions significant. However, two-factor interactions could not be differentiated from three-factor interactions with the data available, as was pointed out earlier.

Graphical Representation of Main Effects and Interactions

The relationship between the total yields listed in Table VII and the effects and interactions presented in Table X may be represented symbolically by Equation (21),

$$Y = \overline{Y} + \sum_{i=1}^{5} \frac{E_i X_i}{2} + \sum_{i=1}^{5} \sum_{j=i+1}^{5} \frac{I_{ij} X_i X_j}{2} \qquad \begin{matrix} (X_i = 1 \text{ or } -1) \\ (X_j = 1 \text{ or } -1) \end{matrix} \qquad (21)$$

where Y = percent yield of oleate or linoleate

$\overline{Y}$ = mean percent yield of oleate or linoleate averaged over all reactions (1F-16F)

E_i = main effect of variable i

I_{ij} = interaction between variables i and j

X_i, X_j = normalized magnitudes of variables i and j

For use in Equation (21), the magnitudes of all variables are normalized such that the high level of any variable has a numerical value of one (1), and its low level has a numerical value of negative one (-1):

$\underline{X_T}$ = magnitude of temperature (1 = 160°C; -1 = 100°C)

$\underline{X_t}$ = magnitude of reaction time (1 = 8 hr; -1 = 2 hr)

$\underline{X_P}$ = magnitude of oxygen pressure (1 = 3500 kPa; -1 = 690 kPa)

$\underline{X_A}$ = magnitude of alkali (1 = $NaHCO_3$; -1 = NaOH)

$\underline{X_S}$ = magnitude of substrate (1 = cotton linters; -1 = wood meal)

If Equation (21) is modified to include only significant effects or interactions, as determined by the analysis of variance, and if linear relationships are assumed between the level of each variable and the total fatty acid yields, then the expected yields of oleate ($\underline{Y_O}$) and linoleate ($\underline{Y_L}$) may be approximated by Equations (22) and (23), respectively.

$$Y_O = 57.0 - (18.7/2)X_T - (13.1/2)X_t - (12.4/2)X_P - (32.4/2)X_A - (3.9/2)X_S - (9.0/2)X_TX_P + (15.4/2)X_PX_S - (18.9/2)X_AX_S \quad (22)$$

$$Y_L = 40.1 - (11.8/2)X_T - (12.8/2)X_t - (13.9/2)X_P - (31.3/2)X_A - (13.8/2)X_S + (12.1/2)X_TX_A + (10.4/2)X_PX_S - (20.5/2)X_AX_S \quad (23)$$

Equations (22) and (23) may be employed to predict the yields of oleate and linoleate as the normalized magnitudes of the variables are interpolated between their high and low levels ($1 \geq \underline{X_i} \geq -1$).

The main effects of all variables may be illustrated graphically as straight lines corresponding to Equations (22a)-(22e) and (23a)-(23e). Those equations were derived from Equations (22) and (23) by expressing the yields of oleate and

linoleate as functions of each variable independently, while maintaining the normalized magnitudes of the remaining four variables at zero.

$$Y_O(T) = 57.0 - 9.35X_T \quad (22a)$$

$$Y_O(t) = 57.0 - 6.55X_t \quad (22b)$$

$$Y_O(P) = 57.0 - 6.2X_P \quad (22c)$$

$$Y_O(A) = 57.0 - 16.2X_A \quad (22d)$$

$$Y_O(S) = 57.0 - 1.95X_S \quad (22e)$$

$$Y_L(T) = 40.1 - 5.9X_T \quad (23a)$$

$$Y_L(t) = 40.1 - 6.4X_t \quad (23b)$$

$$Y_L(P) = 40.1 - 6.95X_P \quad (23c)$$

$$Y_L(A) = 40.1 - 15.65X_A \quad (23d)$$

$$Y_L(S) = 40.1 - 6.9X_S \quad (23e)$$

The main effects of all variables with respect to the yield of oleate, corresponding to Equations (22a)-(22e), are plotted in Fig. 1. The main effects related to the yield of linoleate, Equations (23a)-(23e), are plotted in Fig. 2. In Fig. 1 and 2, the main effect of a variable corresponds to the difference between the low and high values of the straight line which represents a function of that variable.

Interactions may also be described graphically using expressions derived from Equations (22) and (23). Only terms which include the interacting variables are retained in those expressions. For example, the pressure-substrate interactions related to the yields of oleate and linoleate are described by Equations (22f) and (23f), respectively.

$$Y_O(P,S) = 50.7 - 6.2X_P - 1.95X_S + 7.7X_PX_S \quad (22f)$$

$$Y_L(P,S) = 40.1 - 6.95X_P - 6.9X_S + 5.2X_PX_S \quad (23f)$$

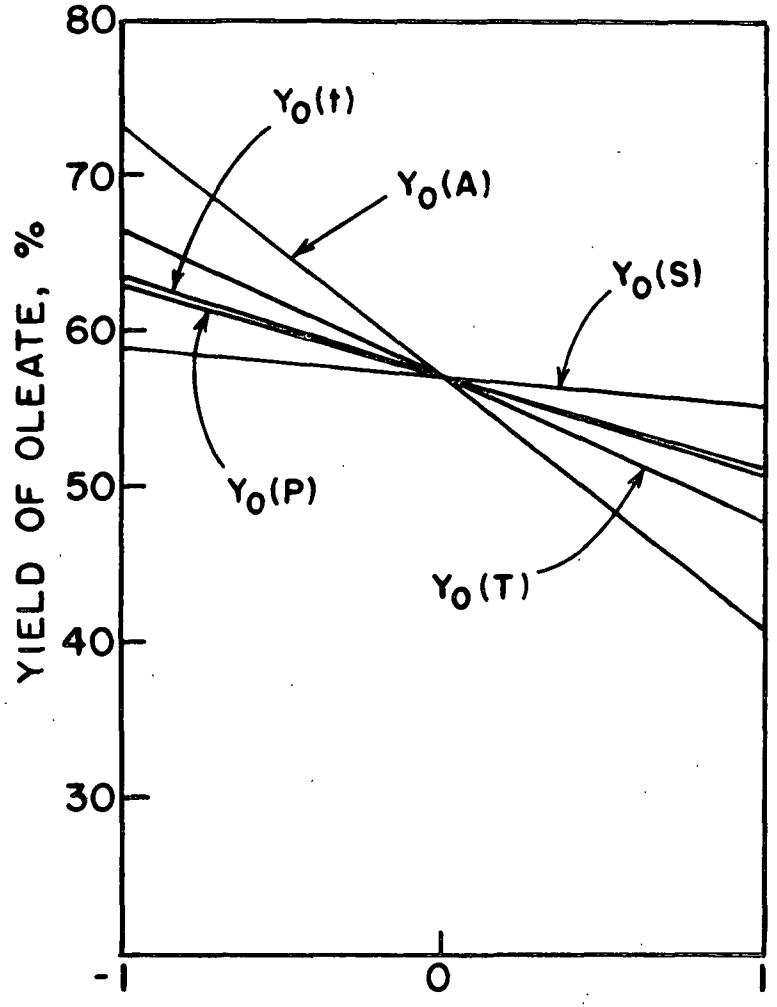


Figure 1. Main Effects of All Variables with Respect to the Yield of Oleate. (Equations 22a - 22e)

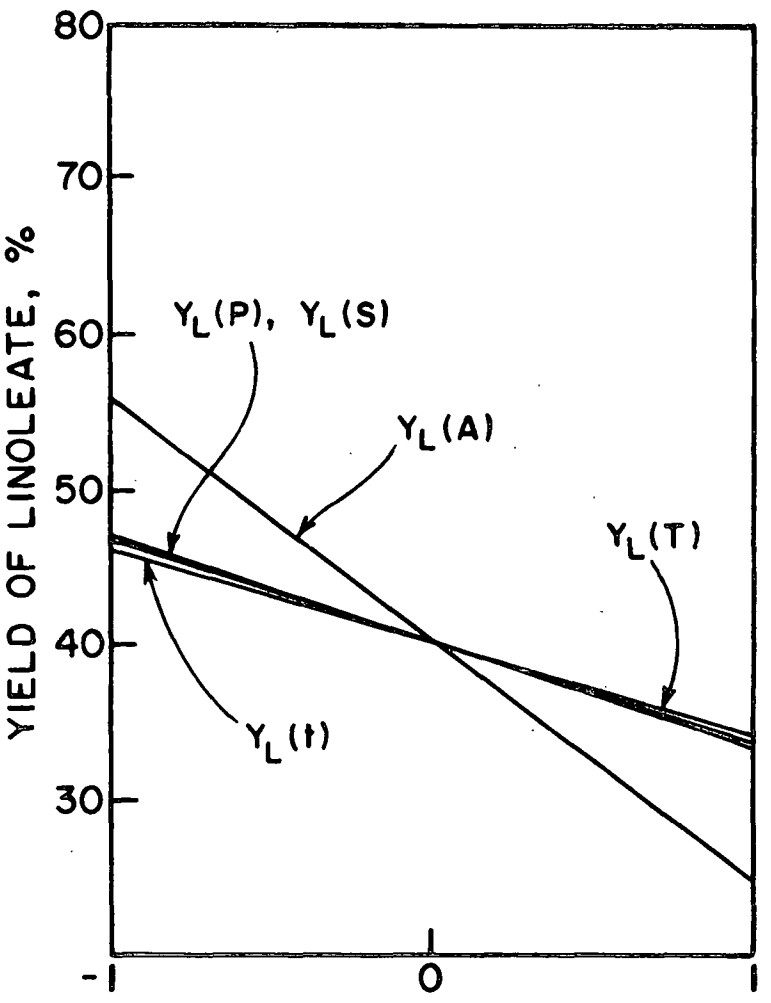


Figure 2. Main Effects of All Variables with Respect to the Yield of Linoleate. (Equations 23a - 23e)

NORMALIZED VARIABLE MAGNITUDE

The oleate pressure-substrate interaction, represented by Equation (22f), is plotted in Fig. 3 and 4. In Fig. 3, the equation is shown as a function of $\underline{X_P}$, while $\underline{X_S}$ is held constant at either its high or low level. Conversely, Fig. 4 shows the same equation plotted as a function of $\underline{X_S}$, with $\underline{X_P}$ maintained at its high or low level. The linoleate pressure-substrate interaction is represented in the same manner by Fig. 5 and 6.

The alkali-substrate interactions for the yields of oleate and linoleate are described by Equations (22g) and (23g), respectively. The oleate-related interaction [Equation (22g)] is plotted in Fig. 7 and 8, while the linoleate-related interaction [Equation (23g)] is represented by Fig. 9 and 10. Again, the figures were derived from the equations by varying each of the interacting variables in turn, while holding the other constant at either its high or low level.

$$Y_O(A,S) = 57.0 - 16.2X_A - 1.95X_S - 9.45X_AX_S \quad (22g)$$

$$Y_L(A,S) = 40.1 - 15.65X_A - 6.9X_S - 10.25X_AX_S \quad (23g)$$

The temperature-pressure interaction related to the yield of oleate is described by Equation (22h). The equation is plotted in Fig. 11 and 12.

$$Y_O(T,P) = 57.0 - 9.35X_T - 6.2X_P - 4.5X_TX_P \quad (22h)$$

The temperature-alkali interaction, which was significant only with respect to the yield of linoleate, is described by Equation (23h). The interaction is plotted in Fig. 13 and 14.

$$Y_L(T,A) = 5.9X_T - 15.65X_A + 6.05X_TX_A \quad (23h)$$

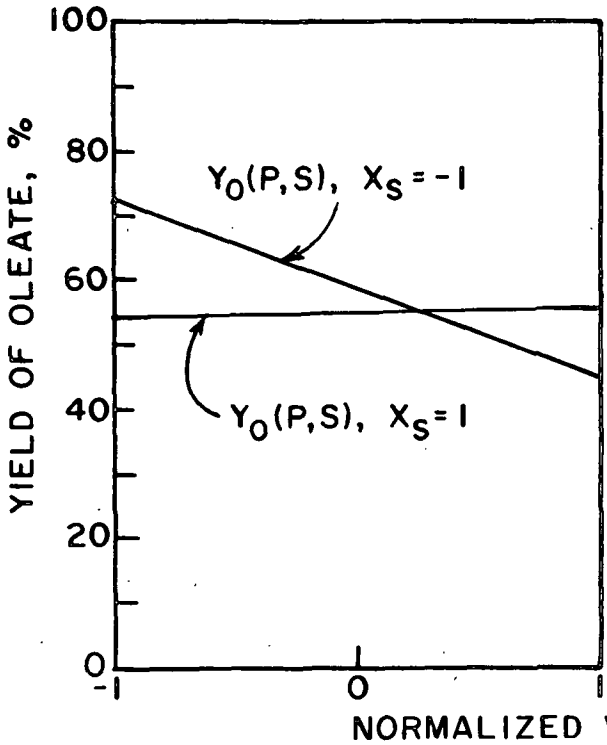


Figure 3. Oleate Pressure-Substrate Interaction. (Substrate Constant)

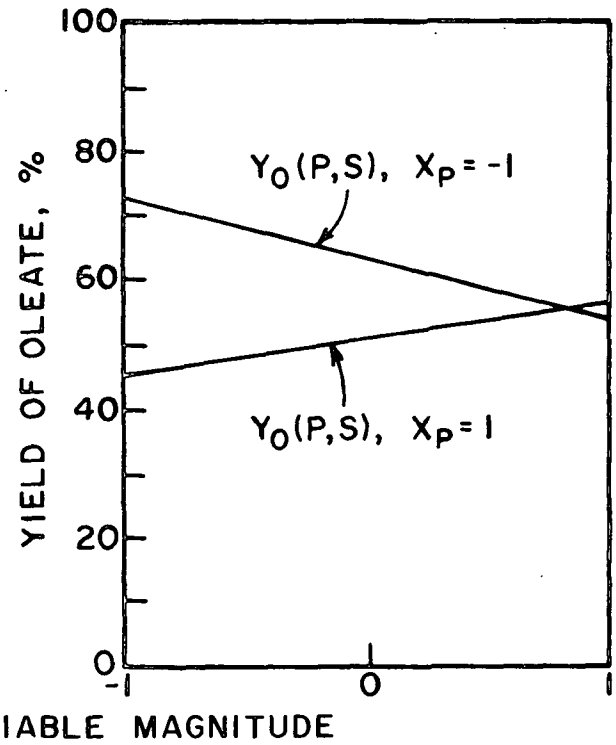


Figure 4. Oleate Pressure-Substrate Interaction. (Pressure Constant)

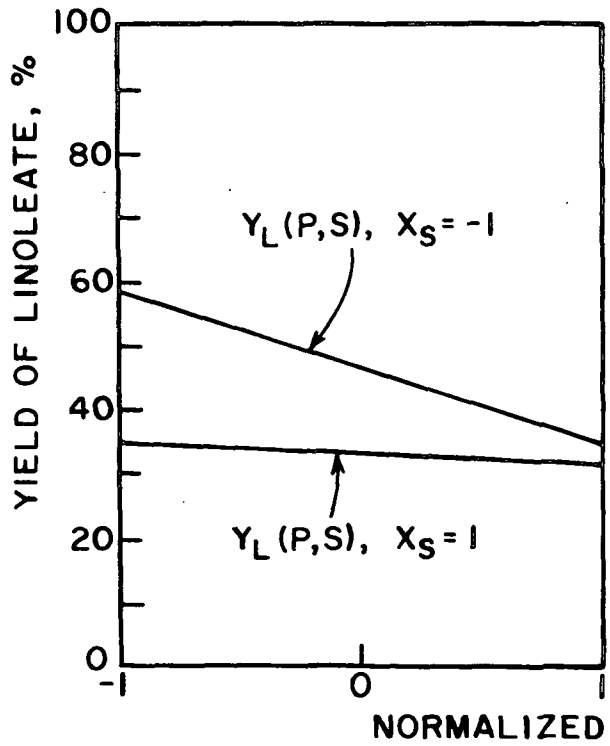


Figure 5. Linoleate Pressure-Substrate Interaction. (Substrate Constant)

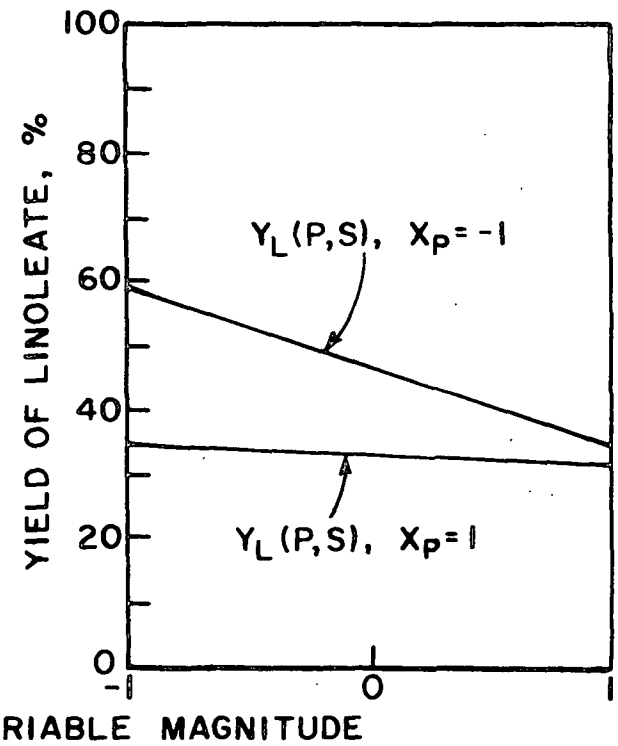


Figure 6. Linoleate Pressure-Substrate Interaction. (Pressure Constant)

NORMALIZED VARIABLE MAGNITUDE

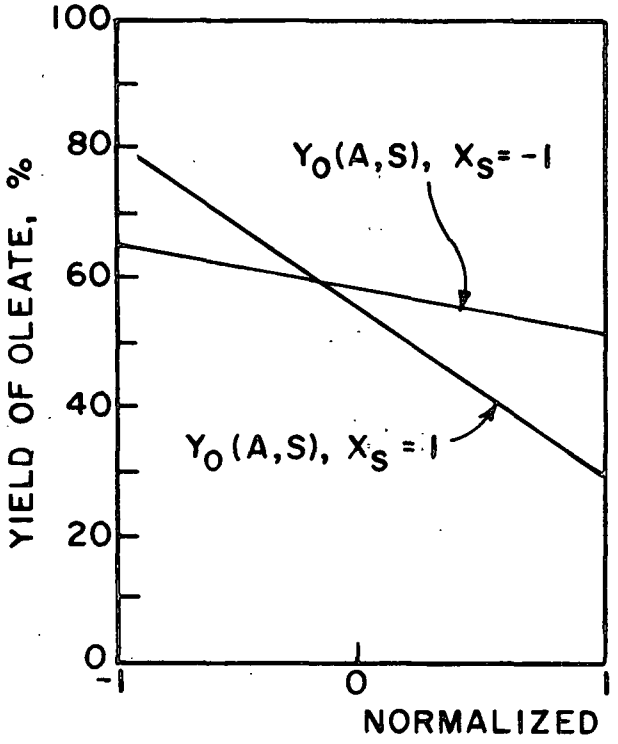


Figure 7. Oleate Alkali-Substrate Interaction. (Constant Substrate)

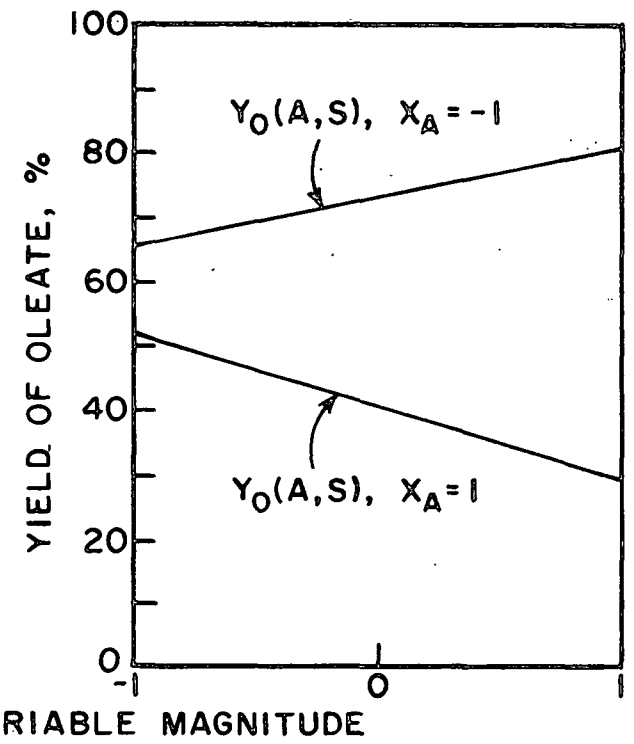


Figure 8. Oleate Alkali-Substrate Interaction. (Constant Alkali)

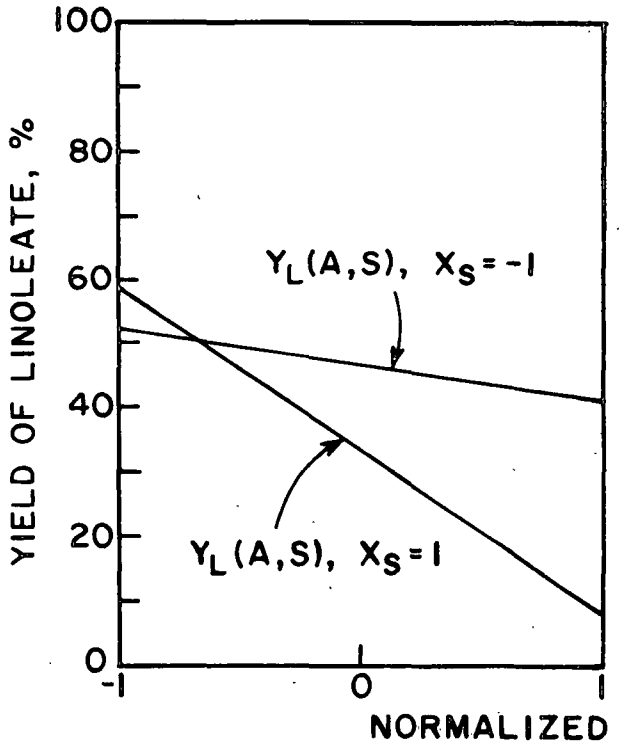


Figure 9. Linoleate Alkali-Substrate Interaction. (Constant Substrate)

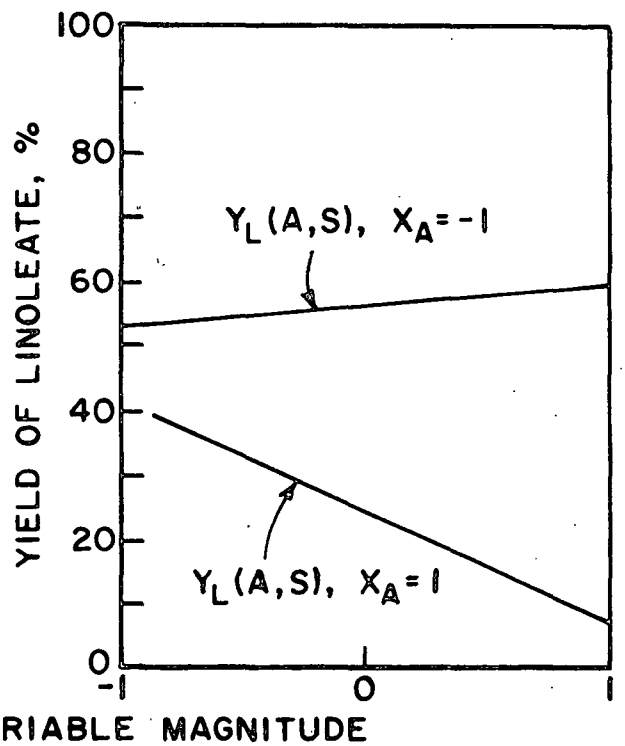


Figure 10. Linoleate Alkali-Substrate Interaction. (Constant Alkali)

NORMALIZED VARIABLE MAGNITUDE

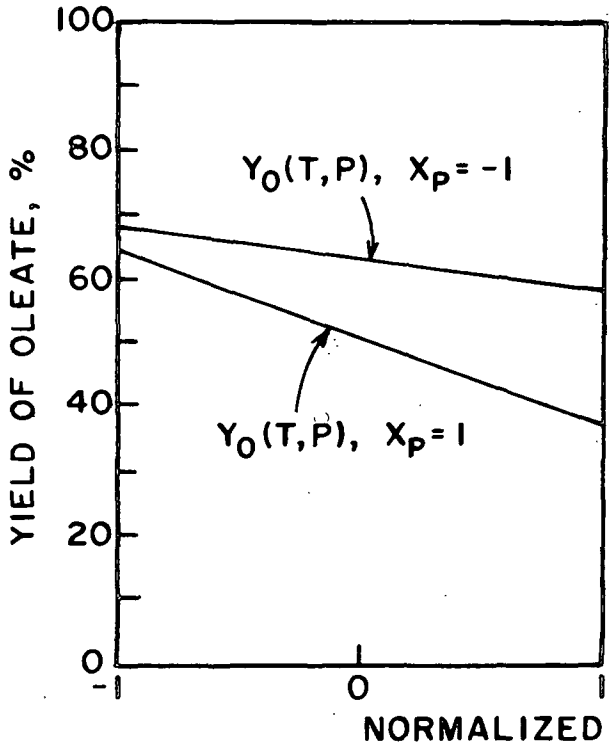


Figure 11. Oleate Temperature-Pressure Interaction. (Constant Pressure)

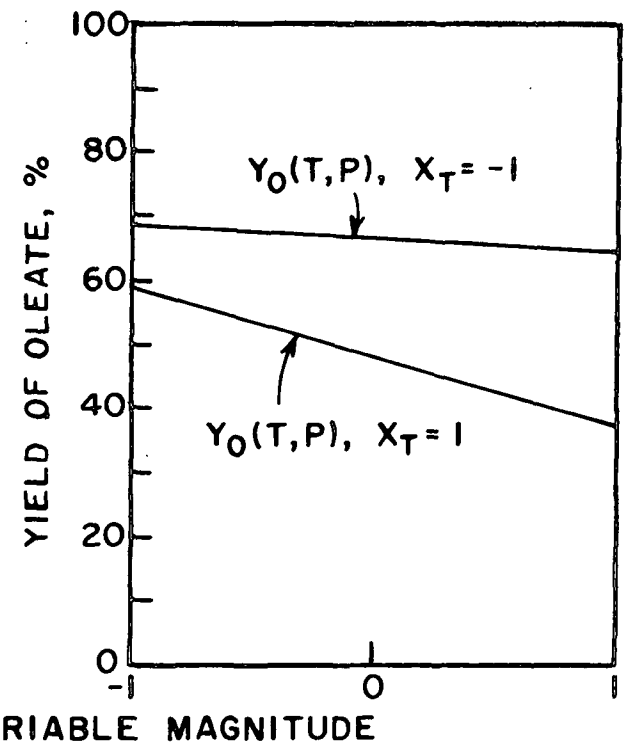


Figure 12. Oleate Temperature-Pressure Interaction. (Constant Temperature)

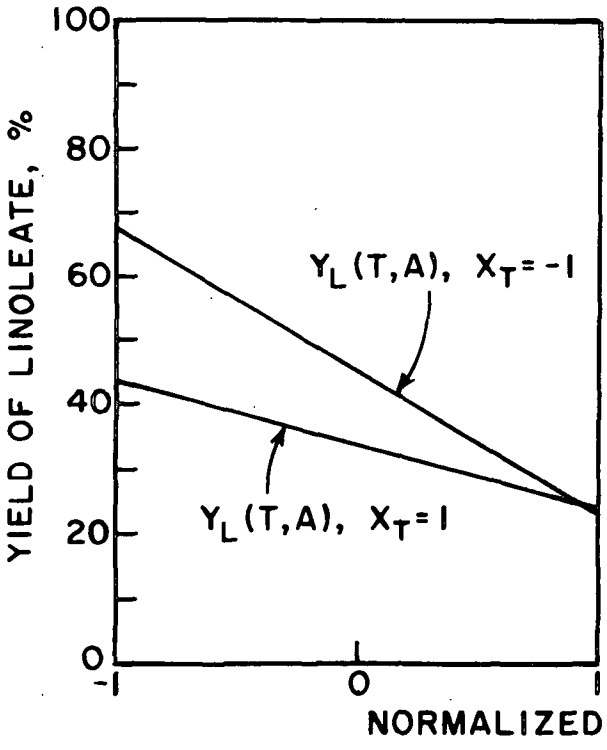


Figure 13. Linoleate Temperature-Alkali Interaction. (Constant Pressure)

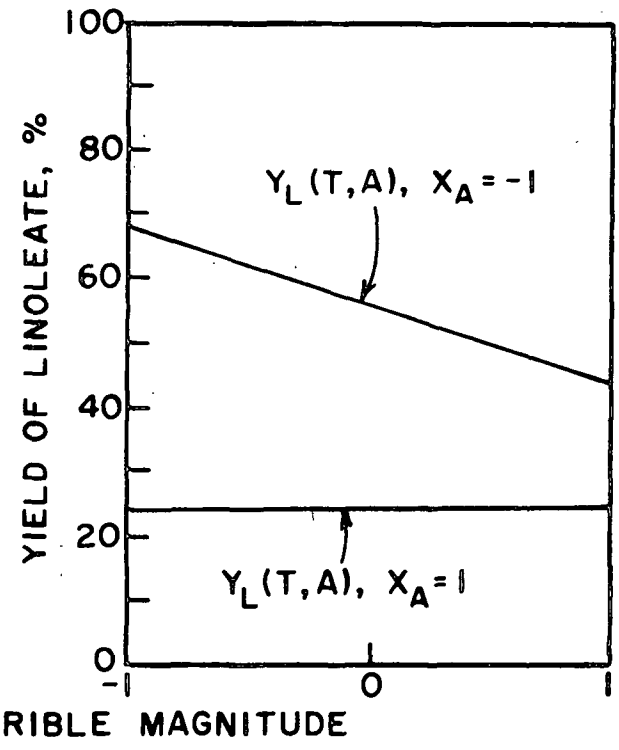


Figure 14. Linoleate Temperature-Alkali Interaction. (Constant Alkali)

In Fig. 3-14, the interactions are shown graphically by the plots obtained when the effects of one interacting variable are determined independently at the high and low levels of the other variable. The magnitude of each interaction is directly proportional to the difference between the slopes of the two functions plotted in each figure. The average slope of the two lines in any figure corresponds to the main effect of a variable. Noninteracting variables would produce parallel lines if their effects were plotted in a similar manner. In all figures, downward sloping lines represent negative effects, while upward sloping lines correspond to positive effects.

If an interaction has a negative effect, then the effect of one variable plotted at the higher level of the other will be more negative than the same effect plotted at the lower level of the second variable. The alkali-substrate interaction related to the yield of oleate, shown in Fig. 7 and 8, has a negative sign and a large magnitude. In Fig. 7, the effect of alkali at the high level of substrate [$\underline{Y}_{\underline{O}}(\underline{A},\underline{S})$, $\underline{X}_{\underline{S}} = 1$] has a much more pronounced negative slope than the effect of alkali at the low level of substrate [$\underline{Y}_{\underline{O}}(\underline{A},\underline{S})$, $\underline{X}_{\underline{S}} = -1$]. Since both plots slope downward, the effects of alkali are negative at both levels of substrate, and only the magnitudes of the two effects differ. Thus, if hydroxide is replaced with bicarbonate, the yield of oleate will decrease in the presence of both wood meal and cotton. However, a much larger decrease will result in the system containing cotton. The main effect of alkali (Table X and Fig. 1) is also negative and has a magnitude which is an average of the two effects observed at the two levels of substrate. Shown in Fig. 8 are the effects of substrate at the two different levels of alkali. When alkali is held at its low level, the plot corresponding to the effect of substrate [$\underline{Y}_{\underline{O}}(\underline{A},\underline{S})$, $\underline{X}_{\underline{A}} = -1$] has a positive slope, showing that the effect of substrate is positive in that system. Therefore, the yield of oleate increases when

wood is replaced with cotton if the alkali is hydroxide. However, the effect of substrate is negative in the presence of cotton, as shown by the downward sloping line obtained when that effect is plotted [$\underline{Y}_{\underline{O}}(\underline{A},\underline{S})$, $\underline{X}_{\underline{A}} = 1$]. The main effect of substrate with respect to the yield of oleate is an average of the negative effect in cotton and the positive effect in wood. As shown in Table X and Fig. 1, the main effect is nearly zero.

The substrate-pressure interaction related to the yield of linoleate, expressed graphically in Fig. 5 and 6, has a positive sign. The effect of either variable is therefore more negative at the lower level of the other. This behavior is clearly demonstrated by the figures. The effect of pressure at the high level of substrate [$\underline{Y}_{\underline{L}}(\underline{P},\underline{S})$, $\underline{X}_{\underline{S}} = 1$] and the effect of substrate at the high level of pressure [$\underline{Y}_{\underline{L}}(\underline{P},\underline{S})$, $\underline{X}_{\underline{P}} = 1$] are represented by nearly horizonal plots. Therefore, pressure has no significant effect in the presence of cotton, and substrate has no significant effect at high pressure. However, the plot corresponding to the effect of pressure when substrate is at its low level, represented by wood meal, has a pronounced negative slope [$\underline{Y}_{\underline{L}}(\underline{P},\underline{S})$, $\underline{X}_{\underline{S}} = -1$]. Similarly, the plot showing the effect of substrate at low pressure slopes markedly downward [$\underline{Y}_{\underline{L}}(\underline{P},\underline{S})$, $\underline{X}_{\underline{P}} = -1$]. Increasing the pressure in the presence of wood, or substituting cotton linters for wood meal at low pressure, causes a significant decrease in the yield of linoleate.

Each of the other interactions plotted may be interpreted in the same manner as the two examples discussed here.

INTERPRETATIONS OF MAIN EFFECTS AND INTERACTIONS

While the results of the half factorial design do not define the optimum conditions for tall oil fatty acid recovery during oxygen-alkali delignification,

some guidelines may be derived from the results which have been presented. Comparisons of the main effects and interactions place emphasis on some factors which should be considered if maximum recovery of fatty acids is desired. In addition, reasonable explanations for the effects and interactions observed may be postulated in most cases.

Review of Main Effects and Interactions

With respect to the yield of oleate, the main effects of all variables except substrate are significant or highly significant. All main effects are significant or highly significant with respect to the yield of linoleate. The main effects are all negative, meaning that fatty acid yields should decrease if a variable is raised from its lower level to its higher level. Alkali has by far the most pronounced effect of any variable. Alkali is also involved in a highly significant interaction with substrate, and substrate further interacts significantly with oxygen pressure. An apparent interaction between temperature and pressure exists with respect to the yield of oleate, while an interaction between temperature and alkali is observed with respect to the yield of linoleate.

Temperature and Reaction Time

Both temperature and reaction time had approximately the same overall effects on losses of the tall oil fatty acids over the ranges which were investigated. The yields of oleate and linoleate dropped an average of 10 to 20% when the temperature was increased from 100 to 160°C or when the reaction time was extended from 2 to 8 hr. From the perspective of tall oil recovery, therefore, a process operating at low temperature for a long time has no apparent advantage over one involving short reaction times and high temperature.

Most interactions involving time and temperature were insignificant. However, an interaction related only to the yield of oleate apparently existed between

temperature and oxygen pressure. The probability of that interaction resulting from experimental error was only about 5%. There was no obvious explanation to account for the interaction. Furthermore, the temperature-pressure interaction related to the yield of linoleate was insignificant.

Another interaction, this time significant only when related to the yield of linoleate, existed between temperature and alkali. The interaction was insignificant with respect to the yield of oleate, and its origins could be traced to circumstances unique to the reactions of linoleate. The yield of that component was very low in all reactions carried out in the presence of cotton linters and bicarbonate. Four such reactions were conducted, and during two of them, Reactions 10F and 16F, the temperature was 160°C, while during the other two, 11F and 13F, the temperature was 100°C. However, because the linoleate yields were so low in all of them, no significant contribution to the temperature effect could be obtained from their results. The temperature effect measured over all reactions involving cotton therefore possessed a relatively low magnitude. Since an effect of much greater magnitude existed in those reactions carried out with wood meal, an interaction between temperature and alkali was observed.

Oxygen Pressure

The main effect of oxygen pressure is of approximately the same magnitude as the main effects of temperature and reaction time. However, the oxygen pressure effect is dependent upon the nature of the substrate, as shown by the interaction between the two variables. In the presence of wood meal, oxygen pressure exerts a pronounced influence upon the degradation of both oleate and linoleate, while in the presence of cotton the reactions of both compounds appear to be independent of the magnitude of oxygen pressure. The oxygen pressure effect noted in the presence of wood meal could be due to several factors, including diffusivity

and chemical oxygen consumption. The experimental program was not designed to determine the dependence of fatty acid oxidation on the diffusion of oxygen through either substrate or water. In fact, the reactions were carried out at high consistency using wood meal rather than wood chips to minimize the limitations imposed by oxygen solubility and diffusivity. However, the results obtained suggest that the rate of fatty acid autoxidation might be diffusion-limited in the presence of wood meal.

On the other hand, that oxygen pressure dependence may not have been solely a mass transfer effect. Both wood and cotton react with oxygen in the presence of alkali, but the reaction with wood is much more rapid and extensive. To determine if an oxygen deficiency may have developed in those systems containing wood, two supplementary reactions were carried out. Fatty acid impregnated wood meal was oxidized under an initial oxygen pressure of 690 kPa, which corresponded to the low level employed in the half factorial design. Samples of the vapor phase were withdrawn from the reactor and analyzed chromatographically for oxygen, carbon dioxide and carbon monoxide. One of the reactions was carried out at 160°C, and the other, at 100°C. The products of both reactions were not otherwise analyzed. After 5 hr of reaction, the vapor phase of the high temperature oxidation consisted of 74% oxygen, 24% carbon dioxide and up to 2% carbon monoxide, excluding water vapor. The carbon monoxide content could not be precisely determined, since its gas chromatographic retention time was very similar to that of oxygen. After the same period of time, the noncondensible vapor from the low temperature reaction was composed almost entirely of oxygen. In the latter case, the pH drop was apparently not great enough to allow release of carbon dioxide into the gas phase. In neither case was an oxygen deficiency evident; in both reactions oxygen was the most abundant component of the vapor phase, even after allowing for water vapor content.

The oxygen pressure dependency observed in the presence of wood may also be rationalized as a combined effect of mass transfer and chemical reaction with the wood. Localized depletion of oxygen could occur because of the reactions involving wood, and the oxidation rates of the encapsulated fatty acids might thus be dependent upon replenishment of oxygen consumed during those reactions. That replenishment would in turn be dependent upon the rate of oxygen diffusion, which itself would depend on the oxygen pressure. The pressure effect is probably not significant in those systems containing cotton because less extensive reaction with oxygen occurs, and because that substrate possesses a greater surface area to volume ratio than the wood meal. The results obtained suggest that fatty acid autoxidation is not directly dependent upon oxygen pressure between 690 and 3500 kPa in the presence of a cotton substrate.

In order to minimize loss of tall oil fatty acids, a low oxygen pressure would appear to be desirable in a delignification process utilizing raw wood. In such a system, a low oxygen pressure would be even more desirable if the rate of delignification did not show an appreciable dependence upon oxygen pressure. On the other hand, if a highly delignified pulp still contained substantial quantities of tall oil, then the extent of further fatty acid degradation after additional treatment with oxygen and alkali would probably be independent of oxygen pressure.

Alkali

The reactions of oxygen with tall oil fatty acids and their esters are acutely dependent upon the nature of the alkali. Degradation of the acids and esters increases sharply if hydroxide is replaced with bicarbonate. As shown by the alkali-substrate interaction, this effect is much more pronounced in the presence of cotton, but it is nevertheless significant when wood is the substrate as well. Furthermore, the fatty acid esters which are not oxidized do

not undergo saponification in systems containing bicarbonate. The results from one of the preliminary oxidations, Reaction 6 (Tables II and III), indicate that this is also the case when sodium carbonate is the alkali. Thus, even if the fatty acid esters survived delignification with oxygen-bicarbonate or oxygen-carbonate, they would not exist as water-soluble soaps and would probably not be recoverable by conventional means. However, the differences in reactivities between bicarbonate containing systems and hydroxide containing systems do not reflect differences between the reactivities of fatty acid methyl esters and free fatty acids. As will be demonstrated later, the same alkali effect is observed in reaction systems initially containing free fatty acids.

The discrepancy in the alkali effect between reactions carried out in the presence of cotton and those conducted with wood meal may be a manifestation of the extensive reaction which occurs between wood and oxygen in the presence of sodium hydroxide. Cotton also undergoes reaction with oxygen and hydroxide, but the simultaneous pH drop is probably not as rapid or as extensive as that which occurs in wood. The high magnitude of the alkali effect for reactions carried out in the presence of cotton may thus reflect a much higher pH differential than that which exists between those reactions carried out with bicarbonate and hydroxide in the presence of wood.

Consumption of hydroxide may have been so extensive that the active alkali was actually carbonate during the later stages of some wood meal-sodium hydroxide reactions, particularly Reactions 2F and 8F. As was discussed previously, a considerable quantity of carbon dioxide was evolved during a supplementary reaction run with wood, oxygen and sodium hydroxide at 160°C. After the pressure was relieved and the reactor cooled, the pH of the spent liquor was measured. The value recorded was 9.4. Both the presence of carbon dioxide in the gas phase and the relatively low pH of the spent liquor suggested that essentially all of

the hydroxide initially present had been consumed. Comparisons of the reaction conditions and results from two of the preliminary oxidations, Reactions 5 and 6, further suggest that a wood-hydroxide system may in fact evolve into a wood-carbonate system. The results of those two oxidations were presented in Tables II and III. Reaction 5 was carried out with sodium hydroxide, while sodium carbonate was utilized in Reaction 6; all other reaction conditions were identical. The extent of fatty acid oxidation was about the same during each reaction. As was noted before, unoxidized fatty acid esters were only partially saponified by the carbonate. However, almost complete saponification was effected by the hydroxide. Presumably, saponification occurred in the very early stages of the reaction, before the pH had dropped considerably.

Because the hydroxide-promoted reaction between wood and oxygen is much more rapid relative to the reactions of fatty acid soaps or esters with oxygen, reproducibility is poor when fatty acid derivatives are oxidized in such a system. This may be seen by comparing the results from Reactions 17F, 18F and 19F, which were presented in Table VII. Although all reactions were carried out under identical conditions, using equivalent amounts of starting materials, the observed recoveries of the fatty acids varied considerably. However, a relationship existed between the proportion of unoxidized starting compounds recovered as unsaponified methyl esters, and the extent of fatty acid oxidation. The highest percentage of unoxidized starting material recovered as unsaponified methyl esters was measured after Reaction 17F. However, oxidation of the fatty acid esters was most extensive in that reaction. Conversely, the highest yields of unoxidized fatty acid were achieved in Reaction 18F, but the quantities of fatty acid methyl esters recovered were lower than those measured after the other two reactions. These results further supported the correlation between the rate of the pH drop and the extent of fatty acid oxidation. A rapid pH drop would

result in less saponification of the methyl esters and more extensive oxidation. On the other hand, if the pH drop were not as rapid, saponification of the esters would be more complete, and oxidation would be less extensive.

From the standpoint of recovery technology, the alkali effect has very important implications with respect to tall oil recovery. Fatty acid esters extensively react with oxygen in the presence of bicarbonate, while those esters which are not oxidized do not undergo apppreciable saponification. Since water soluble soaps are not formed, the fatty acid esters which survived the oxygen treatment would remain with the pulp after water washing. Tall oil recovery would probably be eliminated in an oxygen-bicarbonate pulping process, and pitch might cause problems during subsequent stages of the papermaking process.

Substrate

The substrate effect, which is manifested as a protective effect of wood, interacts with other effects in an even more complex manner than the alkali effect. Although the main effect of substrate is significant with respect to the yield of linoleate, it is within the limits of experimental error with respect to the yield of oleate. However, when the alkali-substrate interaction is considered, some of the ambiguity associated with the substrate effect is eliminated.

The alkali-substrate interactions related to oleate and linoleate were plotted in Fig. 8 and 10. As shown in those figures, the effects of substrate were negative, and their magnitudes were appreciable for reactions involving only sodium bicarbonate [$\underline{Y}_{\underline{O}}(\underline{A},\underline{S})$, $\underline{X}_{\underline{A}} = 1$ and $\underline{Y}_{\underline{L}}(\underline{A},\underline{S})$, $\underline{X}_{\underline{A}} = 1$]. In the presence of bicarbonate, wood exerted a protective influence on the oxidations of both oleate and linoleate. Higher yields of fatty acids were achieved when cotton was replaced with wood meal. However, the substrate effects were reversed when the

stronger alkali, hydroxide, was used. As shown in Fig. 8 and 10, fatty acid yields increased when wood was replaced with cotton in the presence of hydroxide [$\underline{Y}_{\underline{O}}(\underline{A},\underline{S})$, $\underline{X}_{\underline{A}} = -1$ and $\underline{Y}_{\underline{L}}(\underline{A},\underline{S})$, $\underline{X}_{\underline{A}} = -1$]. This behavior was the opposite of that observed in the presence of bicarbonate. The observed alkali-substrate interaction may have been a consequence of the pH drop which occurred during reactions involving wood, oxygen and sodium hydroxide. In systems containing hydroxide any protective effect of the wood may have been overwhelmed by an alkali effect resulting from that pH drop. Thus, the same factors which accounted for the decreased effect of alkali in the presence of wood may have been responsible for the reversal of the substrate effect.

The protective effect of wood, which was observed only in the presence of bicarbonate, may be due to antioxidant properties of the wood, or it may be a diffusivity effect. During the reactions of wood with oxygen and alkali, phenolic compounds are formed; these represent potential antioxidants which might inhibit autoxidation of the fatty acids and esters. Phenols are among the most common antioxidants associated with conventional fatty acid autoxidation (20,21), and Scholander, et al. (65) identified a number of phenolic compounds in spent liquor from wood delignified with oxygen and alkali. If such compounds derived from the wood are efficient antioxidants, then the alkali-substrate interaction further suggests that the phenols do not inhibit autoxidation as effectively at high pH. Phenols are not ionized in bicarbonate, and they may act as antioxidants only in their unionized states. Since the phenols are ionized by hydroxide, the protective effect of wood may disappear in the presence of the stronger alkali. The phenolate ions are themselves susceptible to reaction with oxygen, however.

On the other hand, the protective effect of wood could also have been a diffusivity effect, as indicated by the large interaction between oxygen pressure and substrate. As shown in Fig. 4 and 6, the protective effect was very pronounced

at low oxygen pressure, but absent at high pressure. These results suggested that the rate of oxygen diffusion might be important for reactions carried out in wood meal. However, the true nature of the protective effect associated with wood is still in doubt. The ambiguous and contradictory results show that more extensive investigation will be required before the substrate effect can be clearly understood.

When interpreting the substrate effect, consideration should also be given to the quantities of each substrate employed. More wood meal (50 g) was used than cotton linters (30 g), for reasons which were discussed previously. One additional reaction was carried out using 50 g of cotton linters. The reaction was conducted under conditions identical to those employed for Reaction 7F, and the same quantities of starting material were initially present. However, the yields of oleate and linoleate, 1.23 g and 1.10 g, respectively, were significantly less than those measured after Reaction 7F. These results suggested that fatty acid yields would decrease in all reactions employing cotton if the amount present were increased. Thus, the main effect of substrate would probably assume an even greater magnitude if the quantity of cotton used were equivalent in mass to the quantity of wood meal. Presumably, the alkali-substrate and pressure-substrate interactions would retain their significance in such a case.

If recovery of tall oil fatty acids is desired during oxygen-bicarbonate pulping of wood, some type of pretreatment, such as an alkaline or solvent extraction, will be required before extensive delignification occurs. The fatty acid esters will be less likely to undergo degradation during the initial stages of delignification because of the protective effect of wood. In oxygen-hydroxide systems, the lignin content does not appear to markedly influence the reactions of fatty acids with oxygen, although the pH drop which may occur in such systems can be detrimental. If a high pH is maintained throughout delignification,

considerable recovery of tall oil fatty acids may be anticipated, even if the pulp is completely delignified. Furthermore, since the esters are saponified at high pH, the tall oil soap can be recovered by conventional means.

Oxidations of Free Fatty Acids

The effects of alkali and substrate on fatty acid oxidation were further investigated in three supplementary reactions. These reactions were carried out using free fatty acids to insure that the effects observed previously did not reflect differences in the reactivities of fatty acid methyl esters and fatty acid soaps. Two reactions were conducted in the presence of cotton at 130°C for 5 hr under an initial oxygen pressure of 2100 kPa. The alkali in the first reaction (22F) was sodium hydroxide, while sodium bicarbonate was used in the second (23F). The third reaction (24F) was carried out in the presence of wood and sodium bicarbonate. All other reaction conditions were identical to those employed in the first two reactions. The starting compounds added in all three reactions were oleic acid and linoleic acid. The yields of unoxidized fatty acids from the three reactions are reported in Table XI.

TABLE XI

OXIDATIONS OF FREE FATTY ACIDS[a]

Reaction No.	Alkali	Substrate	Weights of Free Fatty Acids, g				Percent Yields of Fatty Acids	
			Added		Recovered			
			Oleic	Linoleic	Oleic	Linoleic	Oleic	Linoleic
22F	NaOH	Cotton	1.54	2.23	1.34	1.47	87.0	65.9
23F	$NaHCO_3$	Cotton	1.54	2.23	0.19	0.01	12.3	0.4
24F	$NaHCO_3$	Wood	1.54	2.23	1.24	1.44	80.5	64.6

[a]Reaction temperature = 130°C, reaction time = 5 hr, oxygen pressure = 2100 kPa. Alkali = 11.0 g NaOH or 23.1 g $NaHCO_3$, substrate = 30 g cotton or 50 g wood.

The losses of fatty acids during Reaction 22F, which was charged with sodium hydroxide and run in the presence of cotton, were quite low. However, when the hydroxide was replaced with bicarbonate, as was done in Reaction 23F, almost complete degradation of both oleic acid and linoleic acid was observed. The effect of alkali upon oxidation of the free acids was even greater in magnitude than the effect observed in those reactions conducted with fatty acid methyl esters. The effect of alkali, therefore, cannot be attributed to differences between the esters and free fatty acids.

As shown by the results of the half factorial design, and further proven from the results of Reactions 22F and 23F, bicarbonate systems are more reactive media than those containing hydroxide, with respect to fatty acid autoxidation. Considerable evolution of carbon dioxide occurred during all reactions conducted with bicarbonate, as evidenced by large increases in the gage pressure observed during those reactions. Much higher pressures were attained in the bicarbonate reaction systems than were reached during reactions involving hydroxide at the same temperatures and initial pressures. The higher pressures were apparently due solely to carbon dioxide released from the bicarbonate. A supplementary reaction was run using cotton and sodium bicarbonate at a temperature of 160°C. The initial oxygen pressure was 690 kPa, although the gage pressure rose considerably after the reactor had reached its final temperature. The maximum pressure attained was 1400 kPa. The vapor phase inside the reactor was analyzed by gas chromatography. After 2 hr of reaction, the noncondensible gases consisted of about two-thirds oxygen and one-third carbon dioxide. After 5 hr the carbon dioxide content had increased to 61%, while the oxygen content was 38%. In both cases small quantities of carbon monoxide, about 1%, were also detected.

While no means were available to measure the actual pH during the reactions conducted in this study, Abrahamsson and Samuelson (66) have predicted that the

pH of bicarbonate solutions at 135°C in sealed vessels might vary between 7 and 9, depending upon the partial pressure of carbon dioxide. The initial pH of those reactions carried out using sodium hydroxide was much higher. However, it undoubtedly dropped throughout all reactions, falling more rapidly and to a greater extent in those systems containing wood meal. The differences between the hydroxide and bicarbonate systems, in terms of fatty acid oxidation, probably involve either pH or the concentrations of bicarbonate and carbonate ions. Dissociation of the fatty acids depends on pH, and the equilibrium concentration of free acid is greater at low pH. The alkali effect might demonstrate that free acids and methyl esters are more reactive than ionized soaps. However, because of its magnitude and because it does not appear to discriminate between methyl esters and free fatty acids, the alkali effect also suggests direct participation by carbonate or bicarbonate in the autoxidation reactions. Carbonate radicals can be created from reactions between bicarbonate or carbonate ions and hydroxyl radicals (67), as shown by Equations (24) and (25).

$$HCO_3^- + \cdot OH \longrightarrow \cdot CO_3^{\cdot -} + H_2O \qquad (24)$$

$$CO_{3\,sm}^{-2\,sm} + \cdot OH \longrightarrow \cdot CO_3^- + {}^-OH \qquad (25)$$

When the concentrations of bicarbonate or carbonate are very high, such reactions might contribute to the maintenance of relatively high steady-state concentrations of carbonate radicals. Those radicals in turn might be capable of initiating fatty acid autoxidation. In a system containing only hydroxide, the concentration of carbonate is much lower, particularly during the early stages of reaction. Hydroxyl radicals and other radical species are still created, but they might have a greater tendency to interact directly with the substrate rather than promote fatty acid oxidation.

The substrate effect was also examined further in two of the reactions (23F and 24F) carried out with free fatty acids. The results presented in Table XI indicate that free acids are protected to an even greater extent than methyl esters by the presence of wood. The recoveries of oleic acid and linoleic acid from Reaction 24F were about the same as those obtained from Reaction 22F, which was run in the presence of cotton and sodium hydroxide. The substrate effect was nearly as great as the effect of alkali with respect to the reactions of free fatty acids. The yields of oleate and linoleate were much greater in Reaction 24F than they were in Reactions 20F and 21F. Both of those reactions were carried out under conditions identical to those employed in Reaction 24F, except that the starting compounds were methyl esters instead of free fatty acids. The yields of oleate and linoleate were 41-46% and 31-34%, respectively. The protective action of wood thus appeared to be more effective for free fatty acids than for methyl esters. However, no additional evidence was obtained to support or explain that conclusion.

SUMMARY OF MAIN EFFECTS AND INTERACTIONS

In summary, the most critical variable affecting oxidation of tall oil fatty acids is the alkali. Unsaturated fatty acids and their esters undergo much more extensive degradation in systems containing bicarbonate than in those which contain only hydroxide. This behavior suggests the participation of carbonate radicals in the autoxidation reactions. Wood acts as a very effective antioxidant in the presence of bicarbonate. The protective effect of wood, which is apparently lost in the presence of hydroxide, may involve diffusivity factors, or it may derive from the antioxidant characteristics of lignin-derived phenolic compounds. When ionized by hydroxide, those phenols may lose their antioxidant properties.

The effects of temperature and reaction time on fatty acid oxidation were relatively straightforward. Over the ranges which were investigated, increases in either temperature or reaction time decreased fatty acid yields to about the same extent. Increasing the oxygen pressure also promoted fatty acid oxidation, but this effect was dependent upon the nature of the substrate. Oxygen pressure was a much more critical variable in systems containing wood meal than in those containing cotton linters. That result indicated that fatty acid autoxidation in the presence of wood was diffusion limited to at least some extent.

FATTY ACID OXIDATION PRODUCTS

While hydroperoxides are considered the primary products of fatty acid autoxidation, such compounds are unstable and readily decompose to secondary products, particularly under conditions as severe as were employed during this investigation. No analyses of hydrogen peroxide, hydroperoxides or other peroxides were attempted, although their existence was assumed. Most of the oxidation products detected were secondary autoxidation products, presumably formed by decomposition of hydroperoxides. Many of those compounds were identified during the preliminary stages of the experimental program, which encompassed Reactions 1-10. The reaction conditions and yields of starting material for those reactions were reported in Tables I-III. The products of Reactions 2 and 5 were investigated most intensively. In both cases the reaction products were fractionated by column chromatography, and some intermediate products not detected among the products of other reactions were identified. The results from the preliminary study were complemented by additional analyses of products from some of the reactions associated with the half factorial experimental design. Two additional oxidations of sodium oleate and sodium linoleate were later conducted in aqueous sodium hydroxide solutions without any substrate. Those were designated Reactions 11 and 12, respectively, and both were carried out under very

severe conditions to insure almost complete degradation of the fatty acid soaps. Reactions 1 through 12 were not themselves connected with the half factorial plan, which was represented by Reactions 1F-16F. Reactions 17F-24F were supplementary reactions and were associated with the factorial design. All reaction product mixtures were analyzed by gas-liquid chromatography in order to obtain a better understanding of the reactions which occur during degradation of fatty acids by oxygen and alkali.

OXIDATION PRODUCTS IDENTIFIED

The major fatty acid oxidation products identified included saturated straight-chain carboxylic acids (XIV), dicarboxylic acids (XV), 9,10-dihydroxystearic acid (VI), and a mixture of trihydroxyoctadecenoic acids (XI). These compounds, all of which had been identified previously (9,19,37-49,51,58,59), were found among the products of almost all reactions during this investigation. In strongly alkaline systems, α-hydroxy acids (XXV) and α-hydroxydicarboxylic acids (XXVI) emerged as major reaction products. While compounds of the former type had been previously detected in very small quantities among the products of autoxidized fatty acid esters (55,59), no references reporting prior identification of the α-hydroxydicarboxylic acids were found. Under suitable reaction conditions, ω-hydroxy acids (XXIV) were also recovered in relatively high abundance. Compounds of this type, which had been identified in previous work (19), were formed preferentially in bicarbonate systems. Some minor products, possibly corresponding to intermediate species, were also detected. Compounds of that type which were tentatively identified include ω-aceto acids (XXVII) and γ-keto acids (XXVIII). They were present in very small quantities and were detected only when the reaction products were first fractionated by column chromatography. Identification of some of those compounds was reported previously (51,58,59). Other minor products tentatively identified were α,β-dihydroxy

acids (XXIX) and β,γ-dihydroxy acids (XXX). Numerous other compounds could be detected by gas-liquid chromatography among the products of all reactions. However, the peaks representing those compounds were usually very small and poorly resolved. No other products were identified.

Shown in Fig. 15 are structures of all the products which were identified. In most instances entire series of compounds were found. Only the general structures are reproduced in the figure. For example, dicarboxylic acids containing from four to nine carbon atoms were identified among the fatty acid oxidation products. These are all represented by structure XV, in which the value of n varies from two to seven.

YIELDS OF FATTY ACID OXIDATION PRODUCTS

Oxidation products formed during Reactions 1F-24F were recovered in the strong acids fractions after the neutrals and weak acids had been separated on DEAE Sephadex. The strong acids were converted to their trimethylsilyl derivatives and analyzed by gas-liquid chromatography. After the fatty acid methyl esters and free fatty acids recovered in the neutrals and weak acids fractions had been analyzed, those fractions were combined, saponified and refractionated on DEAE Sephadex. The strong acids recovered were analyzed as their trimethylsilyl derivatives by gas-liquid chromatography also. Additional quantities of ω-hydroxy acids and long-chain hydroxy acids, not saponified during the reactions with oxygen and bicarbonate, were often detected by this procedure.

The quantities of identified reaction products recovered from Reactions 1F-16F and 21F-24F are presented in Tables XII-XVI. Listed in Table XII are the molar and percent yields of selected classes of compounds, including all dicarboxylic acids, α-hydroxy dicarboxylic acids, ω-hydroxy acids, 9,10-dihydroxystearic acid and the trihydroxy octadecenoic acids. These compounds correspond

to uncleaved oxidation products, and cleavage products derived from the carboxyl bearing ends of the fatty acid molecules. The combined percent yields of all those compounds together are also listed in Table XII, as are the molar quantities of oleate and linoleate consumed during each reaction.

OXIDATION PRODUCTS IDENTIFIED

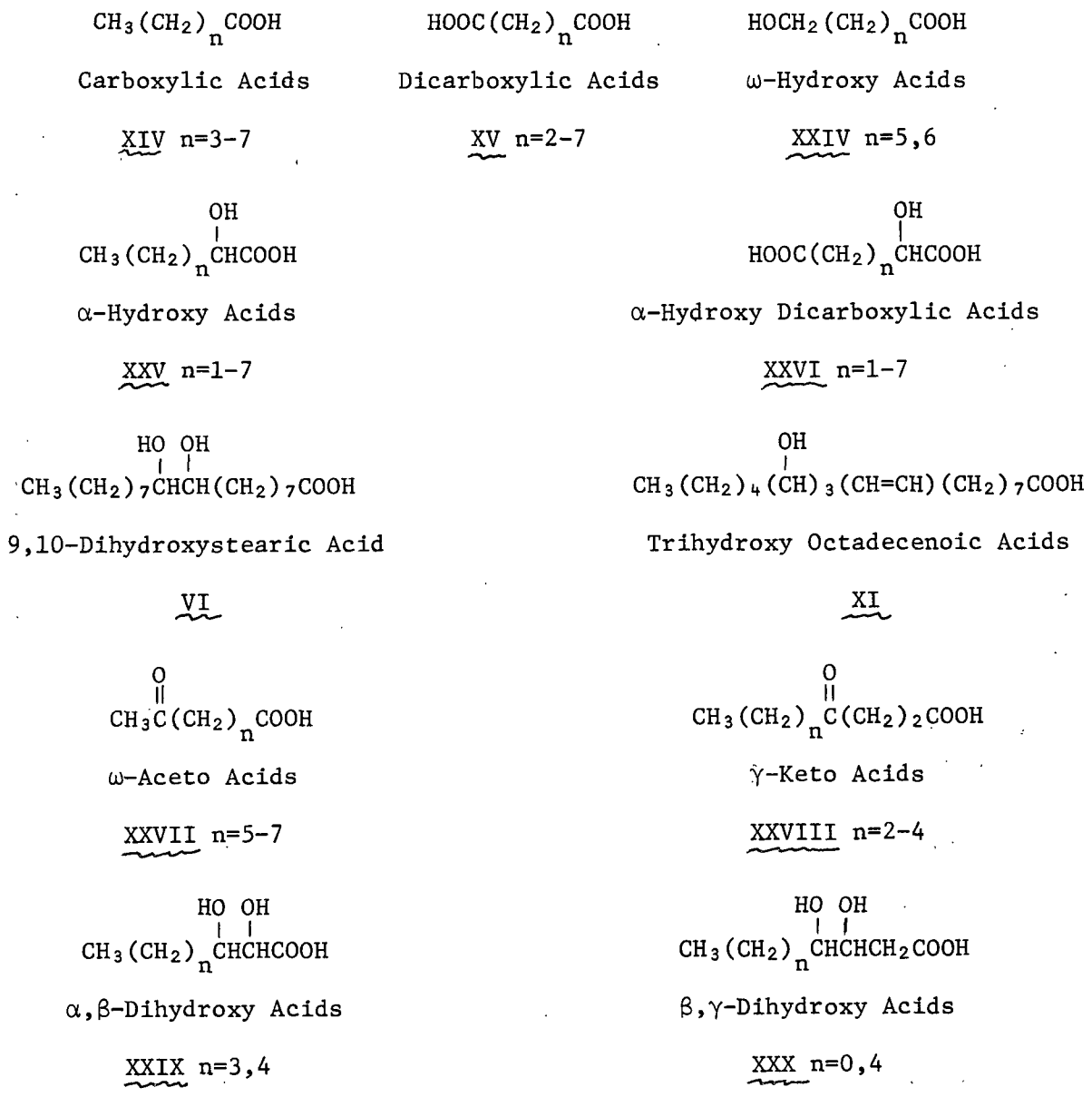


Figure 15. Structures of Fatty Acid Oxidation Products Identified

TABLE XII

OVERALL YIELDS OF OXIDATION PRODUCTS[b]

Reaction No.	Consumed During Reaction[a] (mmole)		Yields of Acidic Oxidation Products								Total Percent Yields
			Dibasic XV		α-Hydroxy Dibasic XXVI		ω-Hydroxy XXIV		Long Chain VI, XI		
	Oleate	Linoleate	mmole	%	mmole	%	mmole	%	mmole	%	
1F	0.74	1.80	0.13	5.1	0.03	1.2			0.06	2.4	8.7
2F	1.15	2.58	0.66	17.7			0.04	1.1	0.14	3.8	22.6
3F	1.15	2.14	0.38	11.5					0.05	1.5	13.0
4F	1.11	3.64	0.93	19.6	0.26	5.5			0.46	9.7	34.8
5F	1.69	2.88	0.28	6.1					0.04	0.9	7.0
6F	1.52	3.87	0.55	10.2	0.49	9.1			0.22	4.1	23.4
7F	1.11	2.51	0.32	8.9	0.23	6.4			0.06	1.7	17.0
8F	3.98	6.11	3.71	36.8			0.30	3.0	0.60	5.9	45.7
9F	1.11	2.68	0.22	5.8			0.04	1.1	0.15	4.0	10.9
10F	4.52	6.21	2.37	22.1			0.43	4.0	0.24	2.2	28.3
11F	4.42	7.10	3.00	26.0			0.69	6.0	0.21	1.8	33.8
12F	2.90	4.38	2.10	28.8			0.42	5.8	0.20	2.7	37.3
13F	2.26	6.52	2.10	23.9			0.24	2.7	0.41	4.7	31.3
14F	3.95	4.28	2.57	31.3			0.41	5.0	0.36	4.4	40.7
15F	3.12	5.50	2.16	25.1			0.42	4.9	0.11	1.3	31.3
16F	5.20	6.86	4.37	36.2			0.11	0.9	0.18	1.5	38.6
22F	0.71	2.71	0.43	12.6	0.40	11.7			0.09	2.6	26.9
23F	4.78	7.80	2.83	22.5			0.24	1.9	0.32	2.6	27.0
24F	1.06	2.82	0.37	9.6			0.03	0.8	0.17	4.4	14.8

[a] Reactions 1F-16F initially contained 5.80 mmole methyl oleate and 7.20 mmole methyl linoleate; reactions 22F-24F initially contained 5.45 mmole oleic acid and 7.95 mmole linoleic acid.

[b] The conditions for reactions 1F-16F were listed in Table V, while those for reactions 22F-24F were presented in Table XI.

Of the fatty acids and fatty acid esters which underwent oxidation, only about a third could be accounted for in most instances. The most commonly detected oxidation products were dicarboxylic acids, ω-hydroxy acids and long-chain hydroxy acids, which included 9,10-dihydroxystearic acid and the trihydroxy-ocatadecenoic acids. Nonanedioic acid (XV, n=7) was usually the single most abundant product found. Monocarboxylic acids probably represented major products of all reactions as well. Heptanoic acid (XIV, n=5), octanoic acid (XIV, n=6)

and nonanoic acid (XIV, n=7) were all detected in appreciable quantities when substantial degradation of methyl oleate occurred. However, the lower carboxylic acids, potential oxidation products of methyl linoleate, were not easily detected by the gas chromatographic procedures employed, and none of those compounds was included in the overall yield determinations. For reactions carried out in the presence of cotton and sodium hydroxide, α-hydroxy acids and α-hydroxydicarboxylic acids were also major products. In addition to products which were identified and incorporated into the material balances, numerous other compounds could be detected in small quantities by gas chromatography. Most of those compounds were not identified, and although they may have represented a substantial contribution to the material balance as a group, they were not considered in the yield determinations.

The weights of individual mono- (XIV) and dibasic (XV) carboxylic acids are listed in Table XIII, while the same data are presented as millimoles in Table XIV. Presented in Table XV are the recoveries, in both milligrams and millimoles, of the individual ω-hydroxy acids (XXIV), 9,10-dihydroxystearic acid (VI) and trihydroxyoctadecenoic acids (XI) from all reactions. Similarly, the yields of individual α-hydroxy acids (XXV) and α-hydroxydicarboxylic acids (XXVI) are listed in Table XVI on weight and molar bases. Data in the latter table are taken from Reactions 1F, 4F, 6F, 7F and 22F only, since the α-hydroxy mono- and dibasic acids are not significantly abundant products in any other reactions.

The total yields of reaction products, listed in Table XII, were quite low, and yields of individual compounds seldom exceeded 10%. Total yields of 30 to 40% were commonly measured when the fatty acid esters underwent considerable oxidation, but the total product yields were usually much less, sometimes falling below 10%, when the extents of reaction were relatively low. This discrepancy could have resulted from experimental errors which accumulated

TABLE XIII

WEIGHT RECOVERIES OF MONO- AND DIBASIC CARBOXYLIC ACIDS

Reaction No.	Acidic Reaction Product, milligrams								
	Heptanoic	Octanoic	Nonanoic	Succinic	Pentane Dioic	Hexane Dioic	Heptane Dioic	Octane Dioic	Nonane Dioic
1F							1.0	4.4	16.1
2F				33.7	7.9	1.8	8.8	13.9	30.5
3F				22.6	4.8	1.2	1.6	5.5	10.2
4F				41.9	18.4	5.0	7.8	27.4	34.9
5F				13.8	2.8		3.0	5.8	23.1
6F				11.3	3.6	2.8	9.4	26.7	36.1
7F				3.0	0.8	1.8	4.6	15.2	28.0
8F	11.6	15.1		121.8	34.1	26.8	65.8	126.6	206.1
9F								3.3	37.2
10F	8.6	11.4	17.9	36.9	15.9	16.0	35.7	88.3	207.4
11F	7.1	16.9	38.3	8.3	8.3	5.4	20.4	97.7	403.2
12F				59.7	18.3	14.5	35.8	65.5	141.2
13F				22.6			2.1	35.0	315.7
14F				43.1	8.1	12.7	29.3	84.6	232.8
15F	3.7	6.5	9.7	11.5	3.3	5.0	14.7	69.1	283.5
16F				164.7	61.7	41.7	56.6	120.3	219.4
22F				12.3	2.1	2.7	8.6	23.0	20.8
23F	10.3	21.5	26.9	29.9	14.7	23.7	47.6	128.8	239.3
24F	1.5	1.9		13.1	1.6	1.5	4.7	13.7	23.7

TABLE XIV

MOLAR RECOVERIES OF MONO- AND DIBASIC CARBOXYLIC ACIDS

Reaction No.	Acidic Reaction Product, millimoles								
	Heptanoic	Octanoic	Nonanoic	Succinic	Pentane Dioic	Hexane Dioic	Heptane Dioic	Octane Dioic	Nonane Dioic
1F							0.01	0.03	0.09
2F				0.29	0.06	0.01	0.06	0.08	0.16
3F				0.19	0.04	0.01	0.01	0.03	0.11
4F				0.36	0.14	0.03	0.05	0.16	0.19
5F				0.12	0.02		0.02	0.03	0.12
6F				0.10	0.03	0.02	0.06	0.15	0.19
7F				0.03	0.01	0.01	0.03	0.09	0.15
8F	0.09	0.10		1.03	0.26	0.18	0.41	0.73	1.10
9F								0.02	0.20
10F	0.07	0.08	0.11	0.31	0.12	0.11	0.22	0.51	1.10
11F	0.05	0.12	0.24	0.07	0.06	0.04	0.13	0.56	2.14
12F				0.51	0.14	0.10	0.22	0.38	0.75
13F				0.19			0.01	0.20	1.70
14F				0.37	0.06	0.09	0.18	0.49	1.40
15F	0.03	0.05	0.06	0.10	0.03	0.03	0.09	0.40	1.51
16F				1.40	0.47	0.29	0.35	0.69	1.17
22F				0.10	0.02	0.02	0.05	0.13	0.11
23F	0.08	0.15	0.17	0.25	0.11	0.16	0.30	0.74	1.27
24F	0.01	0.10		0.11	0.01	0.01	0.03	0.08	0.13

TABLE XV

RECOVERIES OF ω-HYDROXY ACIDS AND LONG CHAIN HYDROXY ACIDS

Reaction No.	Acidic Reaction Product: 6-Hydroxy Hexanoic mg	6-Hydroxy Hexanoic mmole	7-Hydroxy Heptanoic mg	7-Hydroxy Heptanoic mmole	8-Hydroxy Octanoic mg	8-Hydroxy Octanoic mmole	9,10-Dihydroxy Stearic mg	9,10-Dihydroxy Stearic mmole	Trihydroxy Octadecenoic mg	Trihydroxy Octadecenoic mmole
1F							6.0	0.02	11.2	0.04
2F			2.0	0.01	4.9	0.03	13.8	0.05	31.7	0.09
3F							8.0	0.03	7.2	0.02
4F							59.4	0.18	98.4	0.28
5F							4.3	0.02	7.7	0.02
6F							36.7	0.11	37.2	0.11
7F							6.1	0.02	13.5	0.04
8F	4.1	0.03	11.1	0.08	31.1	0.19	80.1	0.25	122.2	0.35
9F					7.7	0.04	13.7	0.04	38.1	0.11
10F	5.0	0.04	8.8	0.06	53.1	0.33	31.4	0.09	44.5	0.15
11F	2.5	0.02	18.7	0.13	85.7	0.54	17.9	0.06	53.7	0.15
12F			10.3	0.07	56.6	0.35	41.5	0.13	38.7	0.12
13F					35.9	0.24	26.4	0.08	115.3	0.33
14F	4.6	0.04	7.4	0.05	50.2	0.32	45.9	0.14	74.0	0.22
15F			7.2	0.05	58.0	0.37	14.0	0.04	25.0	0.07
16F			5.1	0.04	11.8	0.07	34.4	0.11	22.7	0.07
22F							15.7	0.05	13.5	0.04
23F	2.8	0.02	11.7	0.08	21.8	0.14	27.9	0.09	78.4	0.23
24F			0.8	0.01	3.6	0.02	11.1	0.04	45.1	0.13

TABLE XVI

RECOVERIES OF α-HYDROXY ACIDS AND α-HYDROXY DICARBOXYLIC ACIDS

Reaction No.	Acidic Reaction Product: 2-Hydroxy Pentanoic mg	2-Hydroxy Pentanoic mmole	2-Hydroxy Hexanoic mg	2-Hydroxy Hexanoic mmole	2-Hydroxy Heptanoic mg	2-Hydroxy Heptanoic mmole	2-Hydroxy Octane-Dioic mg	2-Hydroxy Octane-Dioic mmole	2-Hydroxy Nonane-Dioic mg	2-Hydroxy Nonane-Dioic mmole	2-Hydroxy Decane-Dioic mg	2-Hydroxy Decane-Dioic mmole
1F			1.6	0.01					5.0	0.02	2.6	0.01
4F	8.5	0.07	12.2	0.09	13.1	0.09	7.0	0.04	28.3	0.14	16.9	0.08
6F	17.1	0.15	27.2	0.21	15.1	0.10	13.2	0.07	60.3	0.30	25.3	0.12
7F	3.7	0.03	12.3	0.09	8.0	0.05	5.2	0.03	26.2	0.13	14.3	0.07
22F	8.8	0.07	24.0	0.18	6.8	0.05	9.3	0.05	50.5	0.25	20.8	0.10

during the workup procedure. Losses of both starting material and reaction products were possible during each product analysis. Errors associated with the analytical procedure were discussed previously. As shown by the results presented in Table VI, the quantities of some reaction products actually formed may have been substantially greater than the values measured, and the actual yields of unoxidized starting material may also have been higher than those measured. In particular, incomplete recoveries of highly water soluble oxidation products and the long-chain hydroxy acids were suspected in all reactions. The overall material balance would be more sensitive to errors if the extent of reaction were very low. As shown by the data in Table XII, the overall yields were in general much less when the recoveries of unoxidized starting material were relatively high.

Results from the analyses of Reactions 1F-16F were consistent with those observed during analysis of the control reaction and reported in Table VI. Most of the data in Tables XII-XVI represented the averages of two or three separate analyses. The measured yields of the fatty acids and fatty acid esters were reproducible, and they were often lower than expected. With respect to the recovery of oxidation products, more reproducible values were measured for yields of the higher dicarboxylic acids than were obtained for the yields of other compounds. Substantial variations between samples were often associated with yields measured for compounds such as succinic acid and the long-chain hydroxy acids.

Listed in Table XVII are the recoveries of oxidation products from the supplementary Reactions 17F, 18F, 20F and 21F. Reasonably good agreement was observed between the results of Reactions 20F and 21F. The neutrals and weak acids from these reactions were not saponified and refractionated, so no recovery of long-chain hydroxy acids was measured in either case. Those compounds were

usually not saponified by bicarbonate and were therefore often retained in the neutrals fractions. Higher yields of oxidation products were measured in Reaction 17F than were recorded for Reaction 18F. As shown by the results presented previously in Table VII, oxidation of fatty acids was less extensive in the latter reaction. The analyses of oxidation products from the two reactions were thus consistent with the results reported earlier concerning yields of starting materials. Recoveries of oxidation products were not determined for Reaction 19F.

TABLE XVII

OXIDATION PRODUCTS FROM REACTIONS 17F-21F

Acidic Oxidation Product	Reaction No. and Product Yield							
	Reaction 17F		Reaction 18F		Reaction 20F		Reaction 21F	
	mg	mmole	mg	mmole	mg	mmole	mg	mmole
Hexanedioic	3.6	0.02	2.9	0.01	9.4	0.06	9.0	0.06
Heptanedioic	14.7	0.08	12.2	0.08	26.0	0.16	26.0	0.16
Octanedioic	36.3	0.21	32.5	0.20	73.0	0.42	78.1	0.45
Nonanedioic	83.2	0.47	73.8	0.43	211.4	1.12	220.9	1.18
Total Dibasic	137.8	0.78	121.4	0.72	319.8	1.76	334.0	1.85
7-Hydroxyheptanoic	3.4	0.02	1.7	0.01	10.1	0.07	10.6	0.07
8-Hydroxyoctanoic	10.5	0.07	10.3	0.06	44.0	0.28	49.5	0.31
Total ω-Hydroxy	14.9	0.09	12.0	0.07	54.1	0.35	60.1	0.39
9,10-Dihydroxy-stearic	12.6	0.04	6.5	0.03	N.D.		N.D.	
Trihydroxy Octadecenoic	50.8	0.14	36.4	0.11	N.D.		N.D.	

FACTORS AFFECTING FORMATION OF FATTY ACID OXIDATION PRODUCTS

Although the overall material balances are low for all reactions, and the recoveries of some identified reaction products incomplete, several distinct features and trends of fatty acid oxidation may be inferred from the results presented in the preceding tables. Most significantly, the α-hydroxy acids and α-hydroxydicarboxylic acids accumulate only under strongly alkaline conditions. In those reactions constituting the half factorial design, such conditions were

achieved only in those systems containing both cotton and sodium hydroxide. If the hydroxide were replaced with bicarbonate, or if wood were substituted for cotton, only very small quantities of α-hydroxy acids were detectable. Furthermore, formation of the α-hydroxydicarboxylic acids appeared to compete with formation of the dicarboxylic acids. The relative yields of the latter decreased as production of the former increased, suggesting common precursors.

Not enough information was obtained to assess accurately the influence of other variables on formation of the α-hydroxy mono- and dibasic acids, but some observations merit comment. The relative yields of those compounds were highest in Reactions 6F and 22F. The former reaction was carried out at high temperature and under a high oxygen pressure, while the temperature and pressure were intermediately high during the latter reaction. In each case, 2-hydroxynonanedioic acid (XXVI, n=6) was the single most abundant oxidation product detected. Among those reactions in which they were considered significant reaction products, the lowest relative yields of α-hydroxy acids and α-hydroxydicarboxylic acids were measured among the products of Reaction 1F, which was carried out at low temperature and pressure. Formation of such compounds does appear to be promoted by high oxygen pressures and high temperatures. The yields in Reactions 4F and 7F, the latter of which involved high temperature but low pressure, and the former low temperature but high pressure, were intermediate. Nonanedioic acid (XV, n=7) and 2-hydroxynonanedioic acid were formed in approximately equal quantities during both reactions.

Oxidation of α-Hydroxy Mono- and Dibasic Acids

The α-hydroxy acids and α-hydroxydicarboxylic acids may themselves be oxidized to mono- and dibasic carboxylic acids possessing one less carbon atom as shown in Equations (26) and (27).

$$CH_3(CH_2)_n\underset{\displaystyle OH}{\underset{|}{C}}HCOOH \xrightarrow{O_2} CH_3(CH_2)_nCOOH + CO_2 + H_2O \qquad (26)$$

XXV XIV

$$HOOC(CH_2)_n\underset{\displaystyle OH}{\underset{|}{C}}HCOOH \xrightarrow{O_2} HOOC(CH_2)_nCOOH + CO_2 + H_2O \qquad (27)$$

XXVI XV

Both reactions occur more extensively in the presence of bicarbonate than in the presence of hydroxide. This was shown when mixtures containing 2-hydroxydecanedioic acid (XXVI, n=7) and 2-hydroxydecanoic acid (XXV, n=7) were allowed to react with oxygen and alkali. Two oxidations were carried out in the presence of cotton at high consistency. In both of them, the temperature, reaction time and oxygen pressure were 130°C, 5 hr and 2100 kPa, respectively. One of the reactions was conducted with an alkali charge consisting of sodium hydroxide, while an equimolar amount of sodium bicarbonate was used in the other. In the presence of the stronger alkali only small, barely perceptible, quantities of nonanoic acid (XIV, n=7) and nonanedioic acid (XV, n=7) were formed, while those compounds were recovered in yields of about 30% from the reactions carried out in the presence of bicarbonate. These results demonstrated that even if α-hydroxy acids and α-hydroxydicarboxylic acids were formed during the reactions of fatty acids with oxygen in the presence of wood or bicarbonate, they might undergo further oxidation before they could accumulate to any significant extent in the system.

Effect of Alkali on the Distribution of Oxidation Products

While formation of α-hydroxy acids is promoted by hydroxide, the yields of ω-hydroxy acids apparently increase in the presence of bicarbonate. Shown in Fig. 16 are gas chromatograms of the products recovered from Reactions 22F and

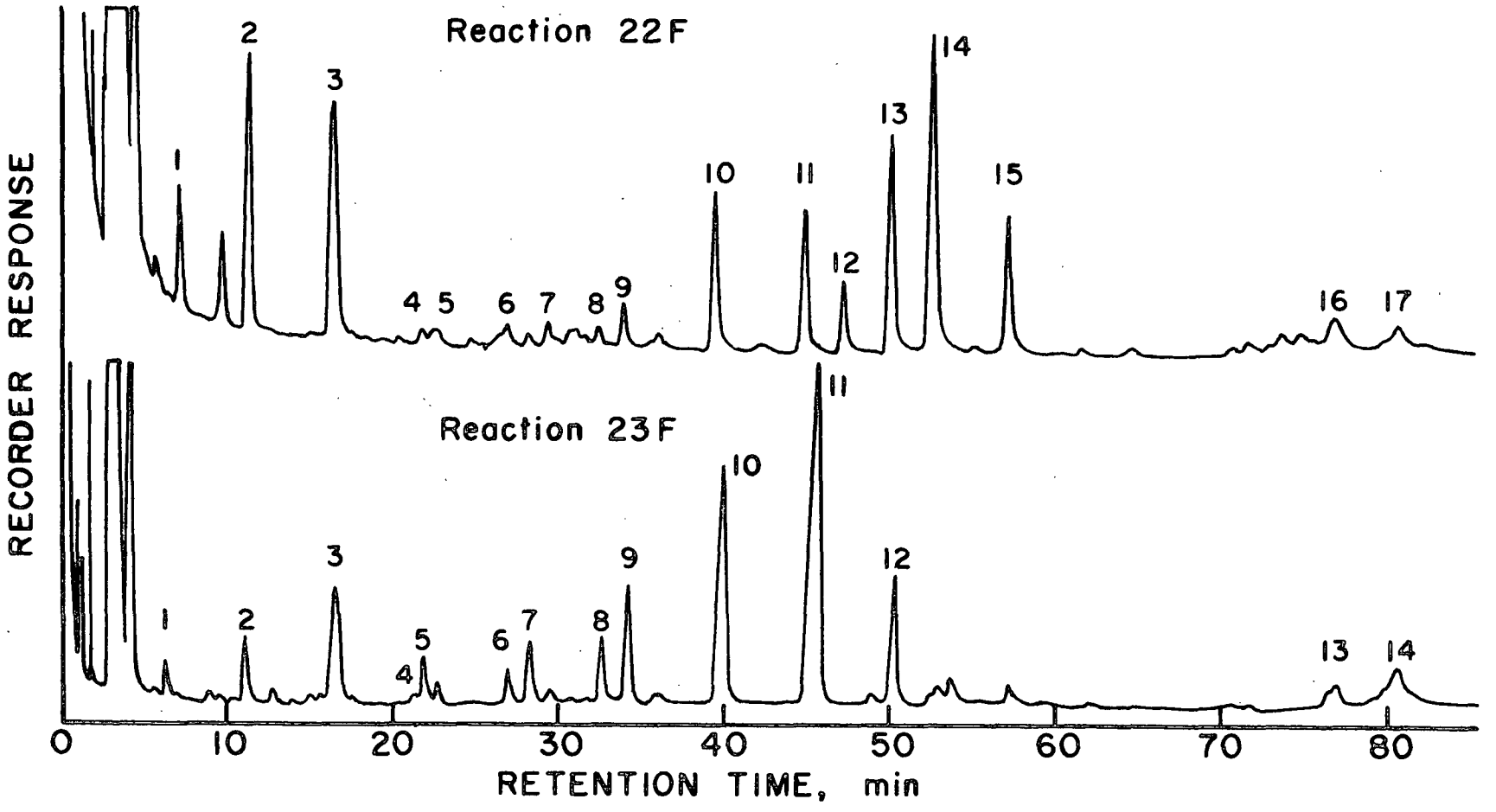


Figure 16. Acidic Oxidation Products from Reactions 22F (Top) and 23F (Bottom). Compounds Separated as Trimethylsilyl Derivatives on OV-17. Numbered Peaks Identified in Table XVIII

23F, each of which involved oxidation of free fatty acids. The reaction conditions and yields of starting material from both reactions were reported in Table XI, while the yields of oxidation products were listed in Tables XII-XVI. Sodium hydroxide was the alkali in Reaction 22F, while sodium bicarbonate was added to Reaction 23F. The peaks numbered in Fig. 16 are identified by number in Table XVIII. Peaks corresponding to decanedioic acid were included in both chromatograms, although twice as much of the internal standard was added to the product of Reaction 23F as to the product of Reaction 22F. Both chromatograms represent 4% of the total reaction products. The trimethylsilyl derivatives of succinic acid, nonanoic acid and 2-hydroxyheptanoic acid possess very similar retention times on OV-17. The three compounds correspond to peaks 22-3 and 23-3 of Fig. 16, as indicated in Table XVIII. All three compounds are effectively resolved on columns packed with SP-2100, but dicarboxylic acids are not separated from α-hydroxydicarboxylic acids on that liquid phase.

The chromatograms reproduced in Fig. 16 graphically illustrate the effect of alkali upon the distribution of fatty acid oxidation products. As is clearly evident, formation of α-hydroxy acids and α-hydroxydicarboxylic acids is promoted by hydroxide, while ω-hydroxy acids are produced in appreciable quantities only in the presence of bicarbonate. Dicarboxylic acids and long-chain hydroxy acids are detected among the products of both reactions. However, the relative amount of nonanedioic acid found is less in the hydroxide reaction.

TABLE XVIII

GAS CHROMATOGRAPHIC PEAK IDENTIFICATIONS FOR FIGURE 16

Peak No. Reaction 22F	Peak No. Reaction 23F	Acidic Oxidation Product
22-1		2-Hydroxypentanoic (XXV, n=2)
	23-1	Heptanoic (XIV, n=5)
22-2		2-Hydroxyhexanoic (XXV, n=3)
	23-2	Octanoic (XXV, n=6)
22-3		2-Hydroxyheptanoic (XXV, n=4) + Succinic (XV, n=2)
	23-3	Nonanoic (XIV, n=7) + Succinic (XV, n=2)
22-4		2-Hydroxyoctanoic (XXV, n=5)
	23-4	6-Hydroxyhexanoic (XXIV, n=4)
22-5	23-5	Pentanedioic (XV, n=3)
22-6		2-Hydroxynonanoic (XXV, n=6)
	23-6	7-Hydroxyheptanoic (XXIV, n=5)
22-7	23-7	Hexanedioic (XV, n=4)
22-8		2-Hydroxydecanoic (XXV, n=7)
	23-8	8-Hydroxyoctanoic (XXIV, n=6)
22-9	23-9	Heptanedioic (XV, n=5)
22-10	23-10	Octanedioic (XV, n=6)
22-11	23-11	Nonanedioic (XV, n=7)
22-12		2-Hydroxyoctanedioic (XXVI, n=5)
22-13[a]	23-12[a]	Decanedioic (Internal Standard)
22-14		2-Hydroxynonanedioic (XXVI, n=6)
22-15		2-Hydroxydecanedioic (XXVI, n=7)
22-16	23-13	9,10-Dihydroxystearic (VI)
22-17	23-14	Trihydroxy Octadecenoic (XI)

[a]Peaks 22-13 and 23-12 correspond to 1.44 mg and 2.87 mg, respectively, of decanedioic acid internal standard. Each chromatogram represents four percent of the total reaction product.

Effect of Temperature on Distribution of Oxidation Products

Changes in temperature also profoundly influence the formation of fatty acid oxidation products. Examination of the data presented in Tables XII-XVI shows that the distribution of reaction products becomes much more diverse at higher temperatures. Relatively large quantities of the low molecular weight products are produced during oxidations carried out at 130 or 160°C, while the reactions are more selective at 100°C. During those reactions carried out at the lower temperature, cleavage of the fatty acid molecules occurs preferentially

at or near the locations of the original double bonds of the fatty acid molecules. Such trends are not as obviously apparent with respect to the other variables, and substituting hydroxide for bicarbonate, or increasing the reaction time appears to have a similar effect. However, the effects of changing those variables are not nearly as pronounced as the effect of temperature on product distributions. The highest yields of any individual compound were achieved after Reactions 11F and 13F. In each case the molar yield of nonanedioic acid, the single most abundant product formed, approached 20% of its theoretical maximum. Both reactions were conducted at 100°C, but one was carried out at high oxygen pressure for a short period of time, while the other involved low pressure and a long reaction time. The alkali used in both reactions was sodium bicarbonate. The yields of nonanedioic acid were substantially less from all reactions conducted at 160°C, but yields of the lower dicarboxylic acids were correspondingly greater.

Formation and Stability of Long-Chain Hydroxy Acids

Attempts to define those parameters which enhanced formation of the long-chain hydroxy acids were largely inconclusive. Although those compounds were usually formed in moderate quantities during all reactions, accurate measurements of their yields were complicated by a number of factors. The long-chain hydroxy acids may not have been completely recovered during analysis, as was discussed previously. Furthermore, accurate integration of the gas chromatographic peaks representing these compounds was difficult because the peaks tended to be broad and were often not completely resolved from other, unidentified peaks. While the long-chain hydroxy acids appeared to be present in exceptionally high yields among the products of Reaction 4F, they were also prominent products of many other reactions. The long-chain hydroxy acids were probably susceptible to oxidation themselves. 9,10-Dihydroxystearic acid (VI) was synthesized, and the compound was oxidized

at 130°C for 5 hr under an initial oxygen pressure of 2100 kPa in the presence of cotton linters. Two oxidations were performed, one with sodium hydroxide and the other with sodium bicarbonate. The acid was stable in the presence of oxygen and hydroxide under those conditions, but some formation of nonanedioic acid and nonanoic acid was observed in the presence of bicarbonate. More extensive oxidation would be anticipated at higher temperatures or after longer reaction times.

Stability of Dicarboxylic Acids

The dicarboxylic acids, which were present in the products of all reactions, were apparently stable to reaction with oxygen in systems containing either hydroxide or bicarbonate. No formation of lower dicarboxylic acids was observed when nonanedioic acid (XV, n=7) was subjected to the same reaction conditions as those just described for the oxidations of 9,10-dihydroxystearic acid. Although nonanedioic acid may be oxidized to octanedioic acid and lower acids by many common oxidizing agents, no such reactions occurred with oxygen in the presence of either hydroxide or bicarbonate. The dicarboxylic acids were apparently stable end products at intermediate reaction conditions, while some degradation might be expected at higher temperatures and longer reaction times.

OXIDATION OF FATTY ACID SOAP SOLUTIONS AT HIGH TEMPERATURE

Two additional oxidations of sodium oleate and sodium linoleate, designated Reactions 11 and 12, respectively, were carried out in alkaline solutions consisting of 2N sodium hydroxide. Both reactions were run at a temperature of 160°C, under an initial oxygen pressure of 3500 kPa. The oleate reaction was terminated after 12 hr, by which time almost 90% of the starting material had been consumed, while the oxidation of linoleate was essentially complete after 8 hr. Considerable amounts of alkali were consumed. Upon cooling, the pH of each

reaction mixture was 12. The alkaline reaction products were neutralized with acid and then treated with a slight excess of ammonia. The ammonium salts were freeze-dried and converted directly to their trimethylsilyl derivatives. This procedure insured complete recovery of all acidic reaction products. Gas chromatograms of the trimethylsilyl derivatives from both reaction products are reproduced in Fig. 17. The yields of individual oxidation products, represented by numbered peaks in the figure, are listed in Tables XIX and XX.

As shown by the data presented in the tables, considerable amounts of the oxidized matter were unaccounted for, even though the analytical procedure insured minimal losses of nonvolatile compounds. The overall molar yields, obtained by combining the yields of all identified reaction products, accounted for only 34% of the oleate and 54% of the linoleate lost. Because the oxidations were carried out at high pH, α-hydroxy acids and α-hydroxydicarboxylic acids were among the major reaction products. The combined yields of dicarboxylic acids and α-hydroxydicarboxylic acids, compounds representing only carboxyl-bearing ends of the original fatty acid molecules, were 27 and 47% for oleate and linoleate, respectively. The remainder of the missing matter consisted in part of compounds present in very low yields. Both chromatograms shown in Fig. 17 included numerous small peaks representing unidentified oxidation products. Low molecular weight compounds such as lactic acid, glycolic acid or oxalic acid were other probable oxidation products, and they may have been formed in substantial quantities. However, the low molecular weight products were not discernible in the massive peaks which first appeared on the chromatograms.

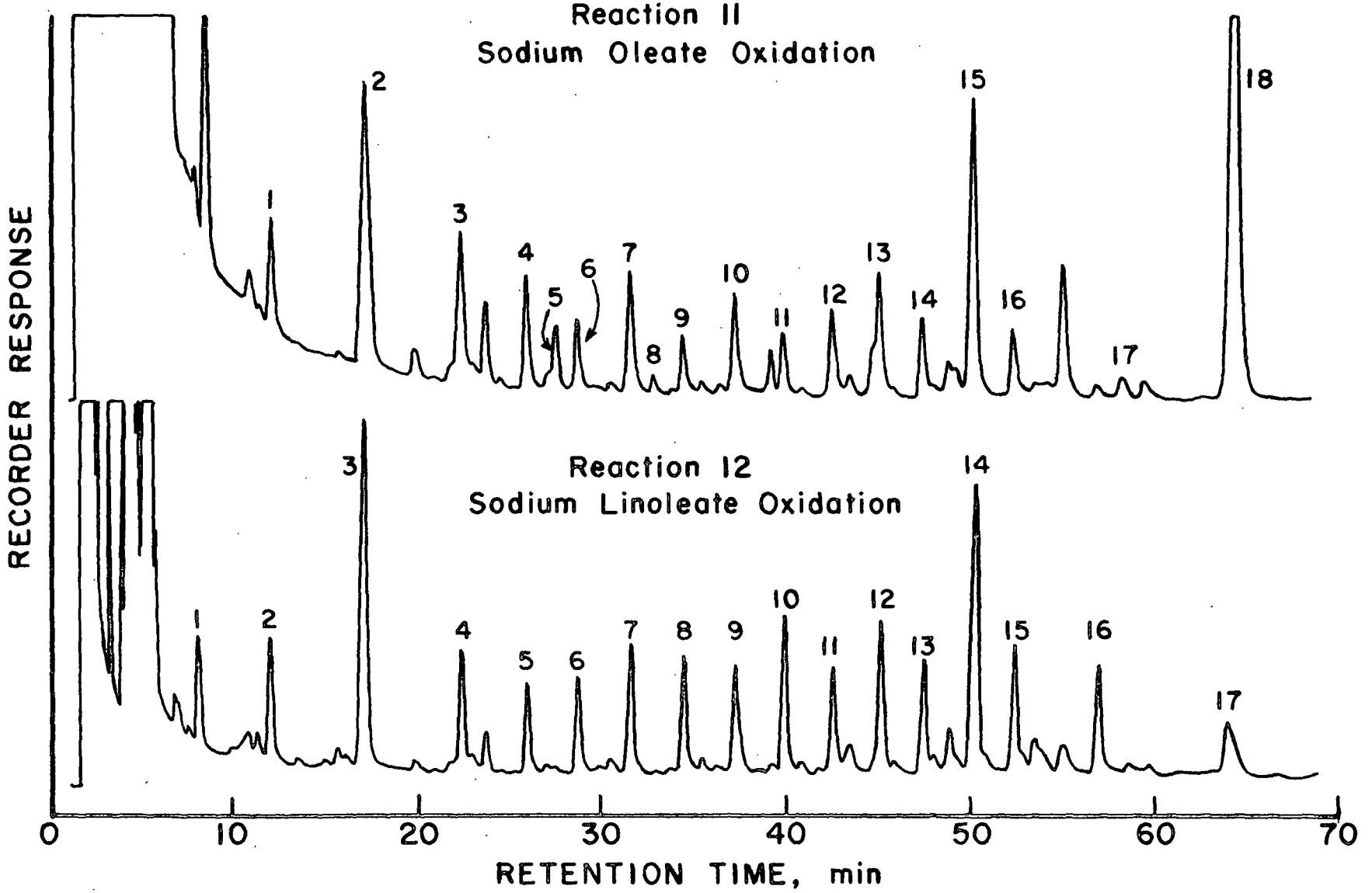


Figure 17. Oxidation Products of Sodium Oleate (Top) and Sodium Linoleate (Bottom). Compounds Separated as Trimethylsilyl Derivatives on OV-17. Numbered Peaks Identified in Tables XIX and XX

TABLE XIX

RESULTS OF REACTION 11. OXIDATION OF SODIUM OLEATE

Compound	Peak No.	Yield mg	Yield mmole	Percent Yield (Molar Basis)
Starting Material				
Oleic acid		1740	6.16	
Linoleic acid		60	0.21	
Unidentified		200	0.7 (as oleic acid)	
Total Starting Material		2000	7.07	
Unoxidized Starting Material				
Oleic acid	11-18	155	0.55	
Linoleic acid	11-18	0	0	
Unidentified		19	0.07 (as oleic acid)	
Total Starting Material Consumed		1826	6.45	
Acidic Oxidation Products				
Octanoic (XIV, n=6)	11-1	10	0.06	0.9
Nonanoic (XIV, n=7)	11-2	14	0.09	1.4
2-Hydroxyhexanoic (XXV, n=3)	11-1	10	0.08	1.2
2-Hydroxyheptanoic (XXV, n=4)	11-2	11	0.08	1.2
2-Hydroxyoctanoic (XXV, n=5)	11-3	8	0.05	0.8
2-Hydroxynonanoic (XXV, n=6)	11-5	11	0.06	0.9
2-Hydroxydecanoic (XXV, n=7)	11-8	4	0.02	0.3
Succinic (XV, n=2)	11-2	39	0.32	5.0
Pentanedioic (XV, n=3)	11-3	23	0.18	3.6
Hexanedioic (XV, n=4)	11-6	15	0.11	1.7
Heptanedioic (XV, n=5)	11-9	13	0.08	1.2
Octanedioic (XV, n=6)	11-11	13	0.07	1.1
Nonanedioic (XV, n=7)	11-13	24	0.13	2.0
Malic (XXVI, n=1)	11-4	29	0.22	3.4
2-Hydroxypentanedioic (XXVI, n=2)	11-7	31	0.21	3.3
2-Hydroxyhexanedioic (XXVI, n=3)	11-10	23	0.13	2.0
2-Hydroxyheptanedioic (XXVI, n=4)	11-12	17	0.10	1.6
2-Hydroxyoctanedioic (XXVI, n=5)	11-14	16	0.08	1.2
2-Hydroxynonanedioic (XXVI, n=6)	11-16	14	0.06	0.9
2-Hydroxydecanedioic (XXVI, n=7)	11-17	2	0.01	0.2
Decanedioic acid (Internal Standard)	11-15			
Total Yield		327	2.14	33.9
Total Yield of Dicarboxylic Acids and α-Hydroxy Dicarboxylic Acids		259	1.70	27.2

TABLE XX

RESULTS OF REACTION 12. OXIDATION OF SODIUM LINOLEATE

Compound	Peak No.	Yield mg	Yield mmole	Percent Yield (Molar Basis)
Starting Material				
Oleic acid		112	0.40	
Linoleic acid		2581	9.20	
Linolenic acid		162	0.58	
Total Starting Material		2855	10.18	
Unoxidized Starting Material				
Oleic acid	12-17	23	0.08	
Linoleic acid	12-17	1	0.01	
Linolenic acid	12-17	0	0	
Total Starting Material Consumed		2831	10.09	
Acidic Oxidation Products				
2-Hydroxypentanoic (XXV, n=2)	12-1	30	0.25	2.5
2-Hydroxyhexanoic (XXV, n=3)	12-2	35	0.27	2.7
2-Hydroxyheptanoic (XXV, n=4)	12-3	23	0.16	1.6
Succinic (XV, n=2)	12-3	104	0.87	8.6
Pentanedioic (XV, n=3)	12-4	58	0.43	4.3
Hexanedioic (XV, n=4)	12-6	48	0.32	3.2
Heptanedioic (XV, n=5)	12-8	55	0.34	3.4
Octanedioic (XV, n=6)	12-10	69	0.40	4.0
Nonanedioic (XV, n=7)	12-12	68	0.36	3.6
Malic (XXVI, n=1)	12-4	38	0.28	2.8
2-Hydroxypentanedioic (XXVI, n=2)	12-7	58	0.39	3.9
2-Hydroxyhexanedioic (XXVI, n=3)	12-9	57	0.35	3.5
2-Hydroxyheptanedioic (XXVI, n=4)	12-11	46	0.27	2.7
2-Hydroxyoctanedioic (XXVI, n=5)	12-13	49	0.25	2.5
2-Hydroxynonanedioic (XXVI, n=6)	12-15	53	0.26	2.6
2-Hydroxydecanedioic (XXVI, n=7)	12-16	46	0.21	2.1
Decanedioic acid (Internal Standard)	12-14			
Total Yield		837	5.41	54.0
Total Yield of Dicarboxylic Acids and α-Hydroxy Dicarboxylic Acids		749	4.73	47.2

Reactions 11 and 12 were conducted at high temperature under a high oxygen pressure for long periods of time. Very little selectivity in the formation of reaction products was observed. As shown by the data in Tables XIX and XX, the yield of no single compound was greater than 9%. The lower dicarboxylic acids and α-hydroxydicarboxylic acids were formed in quantities which sometimes exceeded those of their higher analogues, nonanedioic acid and 2-hydroxynonanedioic acid. Extremely small quantities of the long-chain hydroxy acids were detected among the products of Reactions 11 and 12, although the analytical procedure insured complete recovery of such compounds. The long-chain hydroxy acids were probably formed as a result of reactions between the fatty acid molecules and peroxy radicals (30-33). The concentrations of those species may have been much lower in the soap solutions than in systems containing wood or cotton. On the other hand, long-chain hydroxy acids which might have been formed during Reactions 11 and 12 could have undergone further oxidation because of the severe reaction conditions which were employed. Polymer formation was not evident after either reaction. Both product mixtures consisted of nonviscous, clear solutions when alkaline. Even after acidification, only small quantities of water-insoluble material precipitated. Water solubility was not an expected property of any potential fatty acid-derived polymers.

IDENTIFICATION OF FATTY ACID OXIDATION PRODUCTS

Individual fatty acid oxidation products detected during this investigation were identified exclusively by combined gas chromatography-mass spectrometry. The compounds were analyzed as methyl esters, methyl ester-trimethylsilyl ethers, trimethylsilyl esters, or trimethylsilyl ester-ethers. Compounds of the latter type were also referred to as trimethylsilyl derivatives. Mass spectra were recorded for at least two of these derivatives for most individual compounds. When convenient, identities of the products were proven with the aid of authentic

compounds. Proof of structure was assumed when the gas chromatographic retention time and mass spectrum of an unknown matched those of the authentic compound. The fatty acid oxidation products were predominately acidic. Attempts to isolate and identify neutral products were largely unsuccessful. The only neutral products found were unsaponified esters. Oxidation products of oleate and linoleate were the only compounds identified. The saturated acids underwent only limited reaction with oxygen and alkali, and none of their oxidation products could be detected. Listed in Table XXI are the individual oxidation products which were identified. Compounds were identified specifically by mass spectrometry in those reactions enumerated in the third column of the table. The identities of many of the products were proven with the aid of authentic compounds, as indicated in the last column. Once the identity of a product had been proven, its gas chromatographic retention time was determined. In most of the reactions associated with the half-factorial experimental design, oxidation products were identified only on the basis of the gas chromatographic retention times of their trimethylsilyl derivatives.

MONO- AND DIBASIC CARBOXYLIC ACIDS

Dicarboxylic acids were the most prominent reaction products detected. Nonanedioic acid (XV, n=7) was usually the single most abundant compound formed during oxidation of either oleate or linoleate. The structures of these compounds were first suspected after comparison of the mass spectra of their methyl esters with those published by Ryhage and Stenhagen (68). Authentic specimens of most of the dicarboxylic acids were subsequently obtained to confirm the identifications. Mass spectra of dimethyl esters and ditrimethylsilyl esters were recorded for all the dicarboxylic acids. Shown in Fig. 18 are mass spectra of the dimethyl esters of authentic nonanedioic acid and the same compound recovered from the product of Reaction 2.

TABLE XXI

FATTY ACID OXIDATION PRODUCTS IDENTIFIED

Acidic Oxidation Product		Identification by Mass Spectrometry		
Name	Structure[a]	Identified in Reactions No.[b]	Derivatives Identified[c]	Authentic Compound[c]
Pentanoic	XIV, n=3	10,23F	TMS	
Heptanoic	XIV, n=5	23F	TMS	
Octanoic	XIV, n=6	23F	TMS	
Nonanoic	XIV, n=7	21F,23F	TMS	TMS
Succinic	XV, n=2	5,9,10,12,23F	ME,TMS	TMS
Pentanedioic	XV, n=3	5,10,12,23F	ME,TMS	
Hexanedioic	XV, n=4	5,10,12	ME,TMS	TMS
Heptanedioic	XV, n=5	2,4,5,6,10	ME,TMS	ME,TMS
Octanedioic	XV, n=6	2,4,5,6,10	ME,TMS	ME,TMS
Nonanedioic	XV, n=7	2,4,5,6,9,10	ME,TMS	ME,TMS
2-Hydroxybutyric	XXV, n=1	10,12	TMS	TMS
2-Hydroxypentanoic	XXV, n=2	10,23F	TMS	TMS
2-Hydroxyhexanoic	XXV, n=3	2,5,10,12,23F	ME,ME-TMS,TMS	TMS
2-Hydroxyheptanoic	XXV, n=4	2,5,10,12,23F	ME,ME-TMS,TMS	
2-Hydroxyoctanoic	XXV, n=5	9	TMS	TMS
2-Hydroxynonanoic	XXV, n=6	9	TMS	
2-Hydroxydecanoic	XXV, n=7	9	TMS	TMS
Malic	XXVI, n=1	12	TMS	TMS
2-Hydroxypentanedioic	XXVI, n=2	10,12	TMS	TMS
2-Hydroxyhexanedioic	XXVI, n=3	10,12	TMS	
2-Hydroxyheptanedioic	XXVI, n=4	10,12	TMS	
2-Hydroxyoctanedioic	XXVI, n=5	10,4F	ME-TMS,TMS	
2-Hydroxynonanedioic	XXVI, n=6	2,9,10,4F	ME,ME-TMS,TMS	
2-Hydroxydecanedioic	XXVI, n=7	2,9,10,4F	ME,ME-TMS,TMS	ME,ME-TMS,TMS
7-Hydroxyheptanoic	XXIV, n=5	21F,23F	TMS	
8-Hydroxyoctanoic	XXIV, n=6	21F,23F	TMS	
9,10-Dihydroxystearic	VI	9	TMS	TMS
Trihydroxy Octadecenoic	XI	10	TMS	
7-Oxooctanoic	XXVII, n=5	5	ME	
8-Oxononanoic	XXVII, n=6	2,5	ME	
9-Oxodecanoic	XXVII, n=7	2,5	ME	
4-Oxoheptanoic	XXVIII, n=2	2	ME	
4-Oxooctanoic	XXVIII, n=3	2,5	ME	
4-Oxononanoic	XXVIII, n=4	2,5	ME	
2,3-Dihydroxyheptanoic	XXIX, n=3	10	TMS	
2,3-Dihydroxyoctanoic	XXIX, n=4	10	TMS	
3,4-Dihydroxypentanoic	XXX, n=0	12	TMS	
3,4-Dihydroxynonanoic	XXX, n=4	10	TMS	

[a] Structures of the oxidation products are shown in Fig. 15.
[b] Oxidation products were identified specifically by mass spectrometry in these reactions; refer to Tables I-III, V, VII, XI-XX.
[c] ME = methyl ester; ME-TMS = methyl ester-trimethylsilyl ether; TMS = trimethylsilyl ester or trimethylsilyl ester-ether.

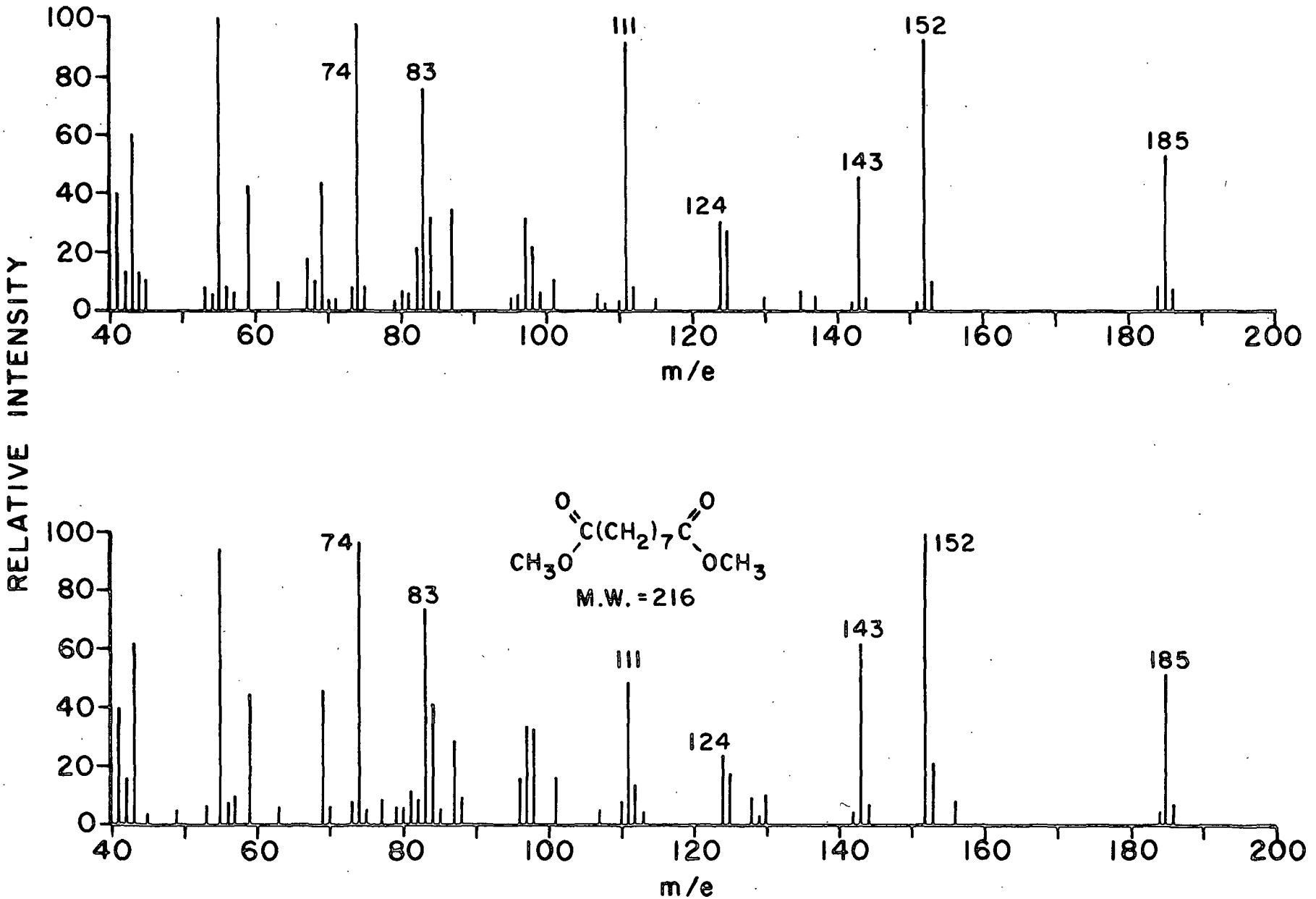


Figure 18. Mass Spectrum of Nonanedioic Acid (XV, n=7) Dimethyl Ester. Top: Compound Recovered in Product of Reaction 2. Bottom: Authentic Compound

Monobasic carboxylic acids are also commonly detected fatty acid autoxidation products. However, some difficulty was encountered in attempts to recover and identify these compounds during this investigation. Both the methyl esters and trimethylsilyl esters of the lower carboxylic acids are quite volatile, and they possess relatively short gas chromatographic retention times. No attempt was made to detect acetic, propanoic or butyric acid. Of the higher acids, only the identity of nonanoic acid was confirmed by comparison with an authentic compound. Pentanoic, heptanoic and octanoic acids were identified only from the mass spectra and gas chromatographic retention times of their trimethylsilyl esters. Hexanoic acid, although undoubtedly an oxidation product of linoleic acid, could not be detected, since the gas chromatographic peak of its trimethylsilyl ester was submerged under the larger peaks of other compounds.

α-HYDROXY MONO- AND DIBASIC CARBOXYLIC ACIDS

The α-hydroxy acids and α-hydroxydicarboxylic acids were prominent products of oxidations carried out at high pH. In some instances one of the latter compounds, 2-hydroxynonanedioic acid (XXVI, n=6), was the single most abundant fatty acid oxidation product detected, exceeding even nonanedioic acid in yield. To aid identification of these compounds, authentic 2-hydroxydecanoic acid (XXV, n=7) and 2-hydroxydecanedioic acid (XXVI, n=7) were synthesized, while several other hydroxy acids were purchased. Reproduced in Fig. 19 and 20 are mass spectra of the dimethyl ester and dimethyl ester-trimethylsilyl ether from authentic 2-hydroxydecanedioic acid. Also shown in the figures are mass spectra corresponding to those derivatives of the same compound recovered from the product of Reaction 2. Mass spectra of trimethylsilyl ester-ethers were also recorded for all α-hydroxydicarboxylic acids identified.

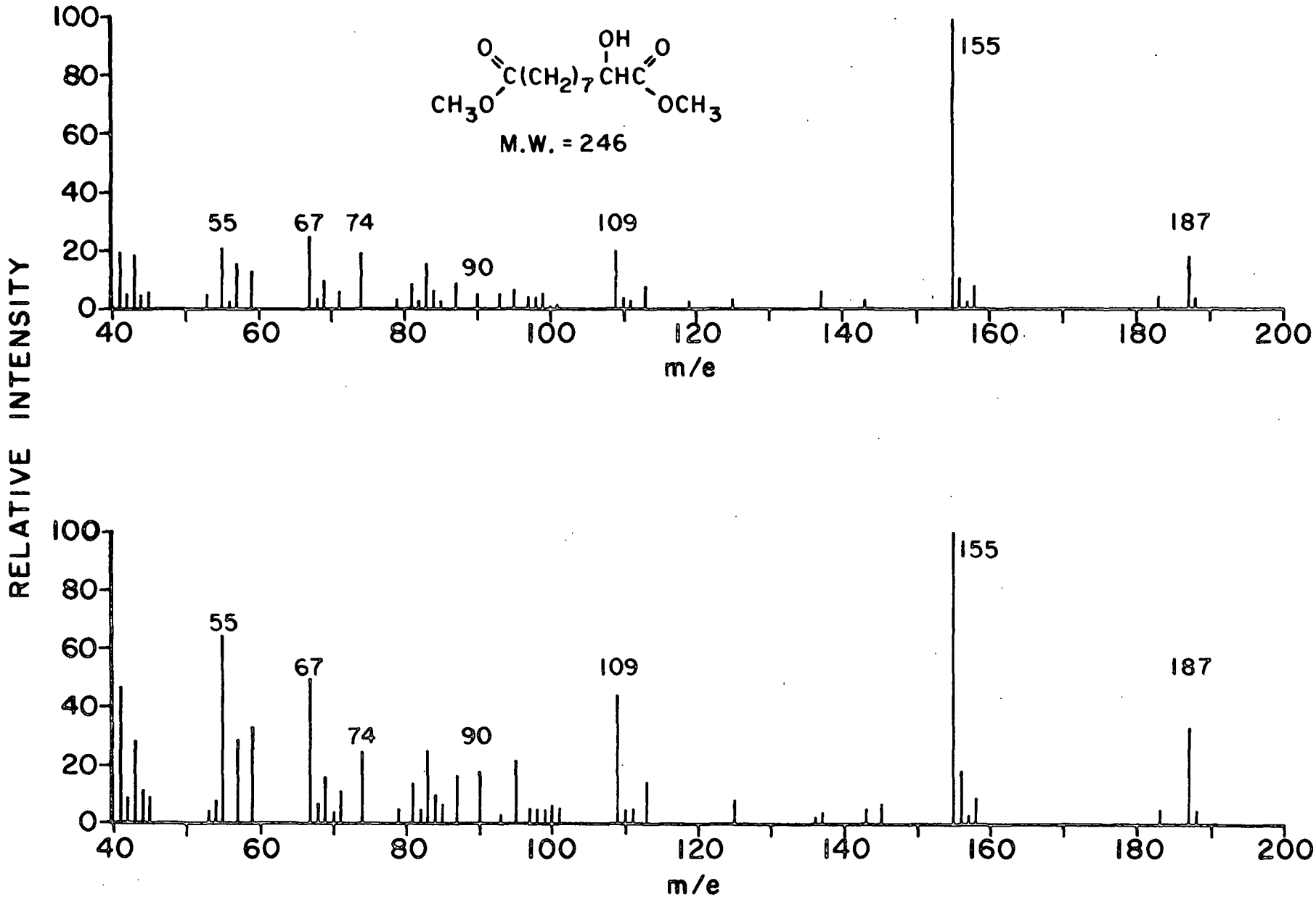


Figure 19. Mass Spectrum of 2-Hydroxydecanedioic Acid (XXVI, n=7) Dimethyl Ester. Top: Compound Recovered in Product of Reaction 2. Bottom: Authentic Compound

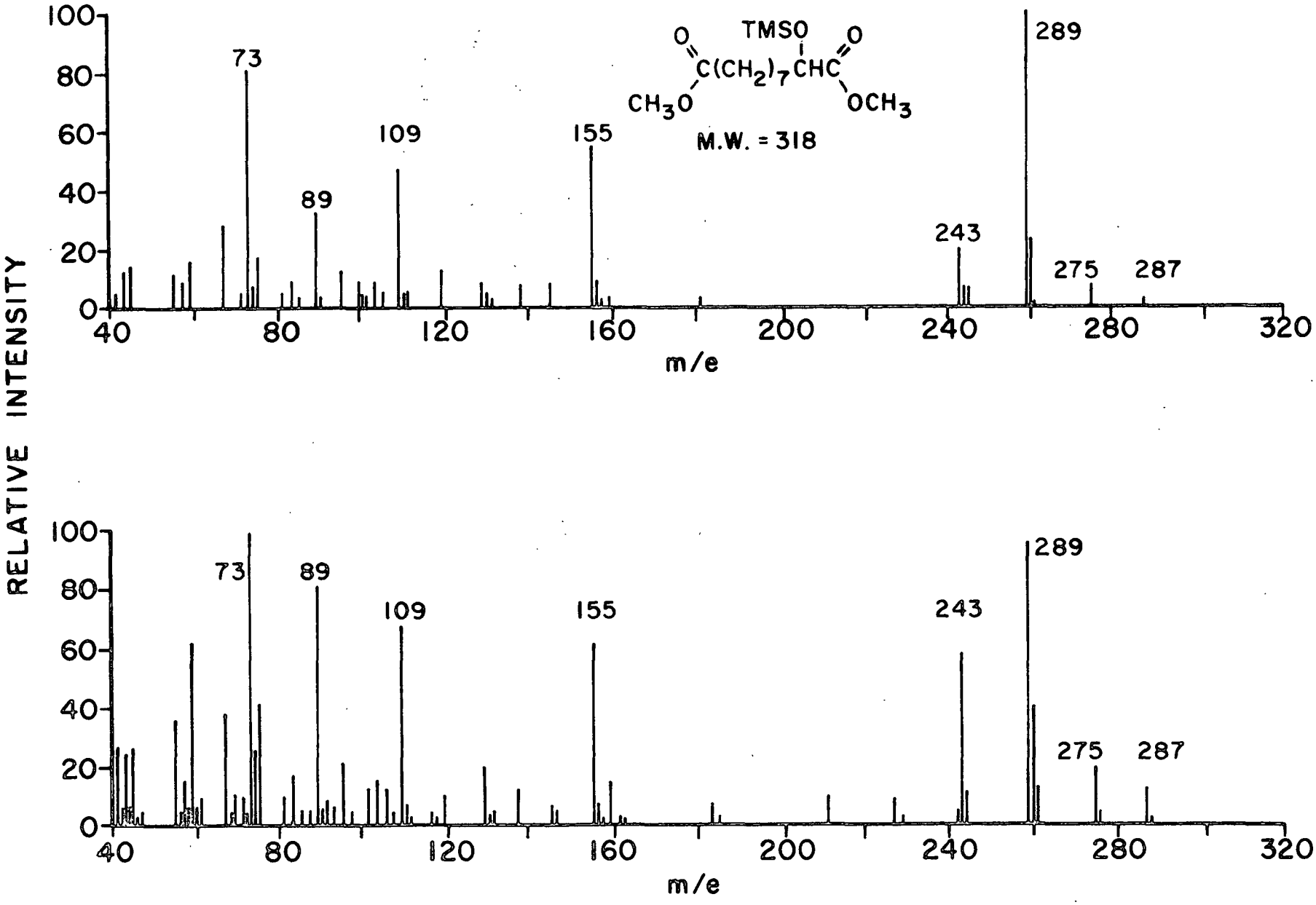


Figure 20. Mass Spectrum of 2-Hydroxydecanedioic Acid (XXVI, n=7) Dimethyl Ester-Trimethylsilyl Ether. Top: Compound Recovered in Product of Reaction 2. Bottom: Authentic Compound

While some α-hydroxy monobasic acids were also analyzed as their methyl esters and methyl ester-trimethylsilyl ethers, the only mass spectra obtained for authentic compounds of this type were from trimethylsilyl ester-ethers. Shown in Fig. 21 are mass spectra corresponding to the trimethylsilyl derivatives of authentic 2-hydroxypentanoic acid (XXV, n=2) and the same compound recovered from the product of Reaction 10.

ω-HYDROXY ACIDS

Oxidation products comprising another class of hydroxy acid were the ω-hydroxy acids. These compounds were normally recovered in appreciable quantities only from reactions run in the presence of bicarbonate. Two such compounds, 7-hydroxyheptanoic acid (XXIV, n=5) and 8-hydroxyoctanoic acid (XXIV, n=6), were identified as their trimethylsilyl derivatives by gas chromatography-mass spectrometry. The existence of another compound of this type, 6-hydroxyhexanoic acid (XXIV, n=4), was suspected from its gas chromatographic retention time only. No authentic specimens of these compounds were obtained, but an analogous compound, 9-hydroxynonanoic acid (XXIV, n=7) was synthesized. Notably, the latter compound was not itself detected among the fatty acid oxidation products. Mass spectra recorded for the trimethylsilyl derivatives of authentic 9-hydroxynonanoic acid and 8-hydroxyoctanoic acid, a fatty acid oxidation product, are reproduced in Fig. 22.

LONG-CHAIN HYDROXY ACIDS

Trihydroxyoctadecenoic acids (XI) and 9,10-dihydroxystearic acid (VI) recovered from the products of Reactions 10 and 9, respectively, were identified as their trimethylsilyl derivatives by gas chromatography-mass spectrometry. Both the threo and erythro isomers of the latter compound were found in the reaction product. The identities of those two isomers were confirmed with the

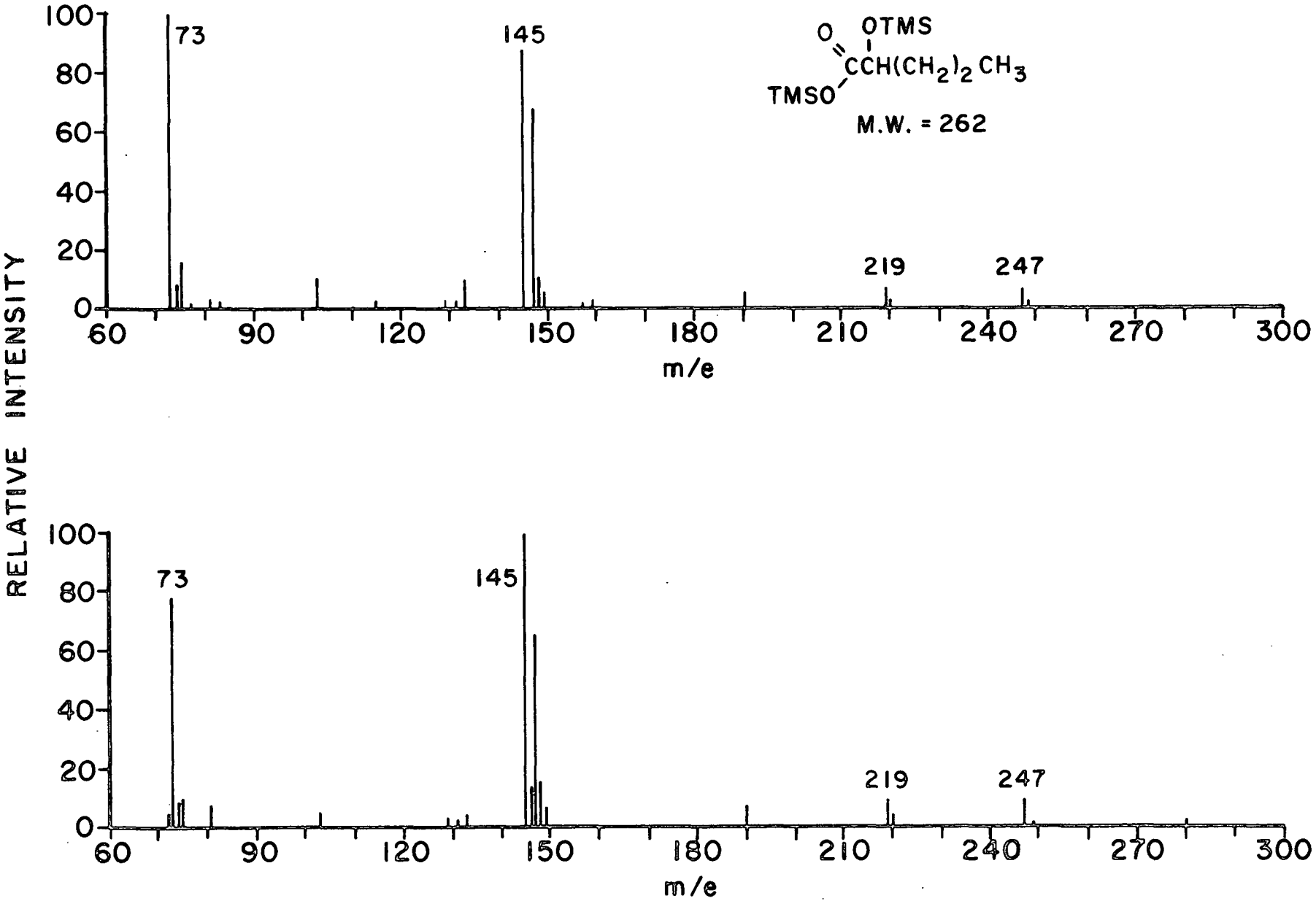


Figure 31. Mass Spectrum of 2-Hydroxypentanoic Acid (XXV, n=2) Trimethylsilyl Derivative.
Top: Compound Recovered in Product of Reaction 10. Bottom: Authentic Compound

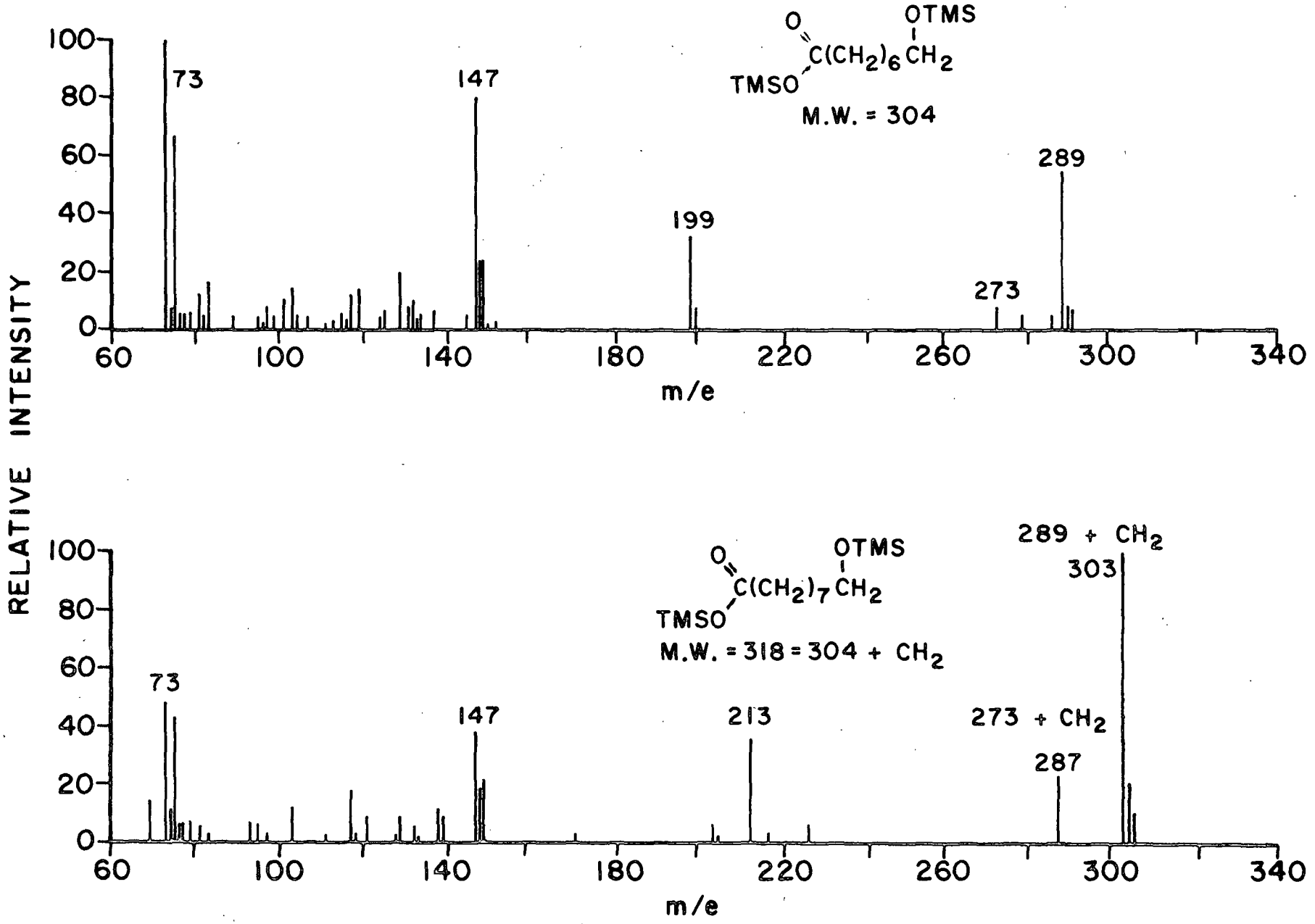
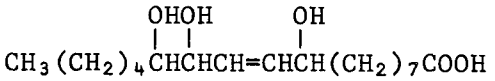
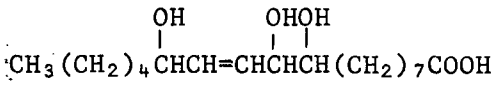


Figure 22. Mass Spectra of ω-Hydroxy Acids. Top: Trimethylsilyl Derivative of 8-Hydroxyoctanoic Acid (XXIV, n=6) Recovered in Product of Reaction 23F. Bottom: Trimethylsilyl Derivative of Authentic 9-Hydroxynonanoic Acid (XXIV, n=7)

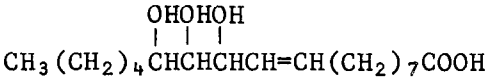
aid of authentic specimens. While mass spectra of the two isomers were indistinguishable, their trimethylsilyl derivatives possessed slightly different gas chromatographic retention times and were differentiated on that basis. No specific structures could be determined for the trihydroxyoctadecenoic acids. While a mixture of isomers was apparently formed during the oxidation of linoleate, these were not adequately resolved to allow procurement of mass spectra corresponding to individual isomers. The compounds did apparently contain three hydroxyl groups and one double bond, as indicated by the general structure XI. Excluding stereoisomers, the general structure may be represented by four unique isomers (XIa-XId):



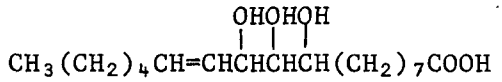
XIa



XIb



XIc



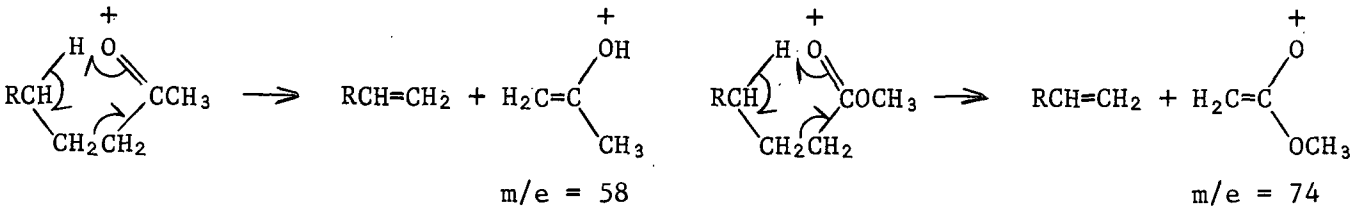
XId

Based on the mass spectra recorded, which are tabulated in Appendix VIII, the most probable structures are those represented by XIa, XIc and XId. Structures XIa and XIb were postulated as linoleic acid oxidation products in previous work (40,48). In those compounds the double bond presumably assumed the trans configuration. The epoxide precursors of structures XIc and XId have also been identified (40,44).

KETO ACIDS

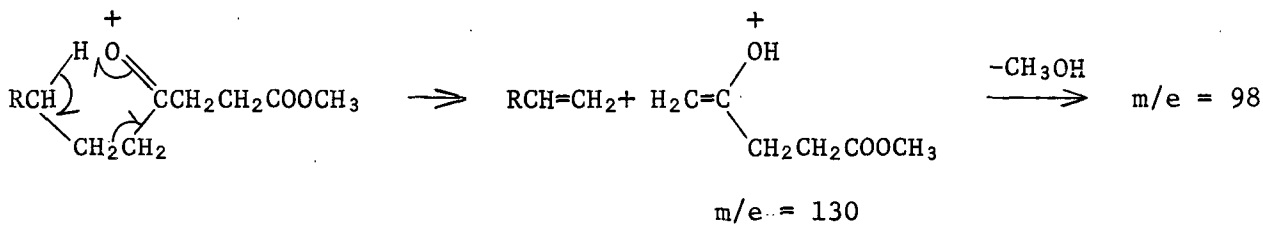
Although authentic specimens of actual reaction products were not obtained, identifications of the ω-aceto acids and γ-keto acids were aided by comparisons of the mass spectra of their methyl esters with those of compounds possessing analogous structures differing only in the number of carbon atoms. Reproduced

in Fig. 23 are mass spectra corresponding to the methyl esters of 9-oxodecanoic acid (XXVII, n=7), a compound found among the products of Reactions 2 and 5, and 17-oxooctadecanoic acid (XXVII, n=15). The mass spectrum derived from the methyl ester of the latter compound was published by Ryhage and Stenhagen (69). Key peaks in both spectra occur at P-15, P-31, P-57, m/e = 43, m/e = 58 and m/e = 74. The latter two peaks correspond to the McLafferty rearrangement ions derived from the aceto and ester carbonyl groups.



Another good diagnostic peak in the spectra of the ω-aceto acid methyl esters is found at P-89, which corresponds to loss of methanol from the P-57 peak.

Mass spectra of the methyl esters of 4-oxooctadecanoic acid (XVIII, n=13) (69) and 4-oxononanoic acid (XVIII, n=4) are reproduced in Fig. 24. The key peaks in both spectra occur at m/e = 130 and m/e = 98. The former peak represents the McLafferty rearrangement ion associated with the keto group, and that ion may lose methanol to yield an ion with a mass-to-charge ratio of 98, corresponding to the latter peak:



Other important diagnostic peaks for the γ-keto acid methyl esters occur at m/e = 87, m/e = 115, P-87 and P-31.

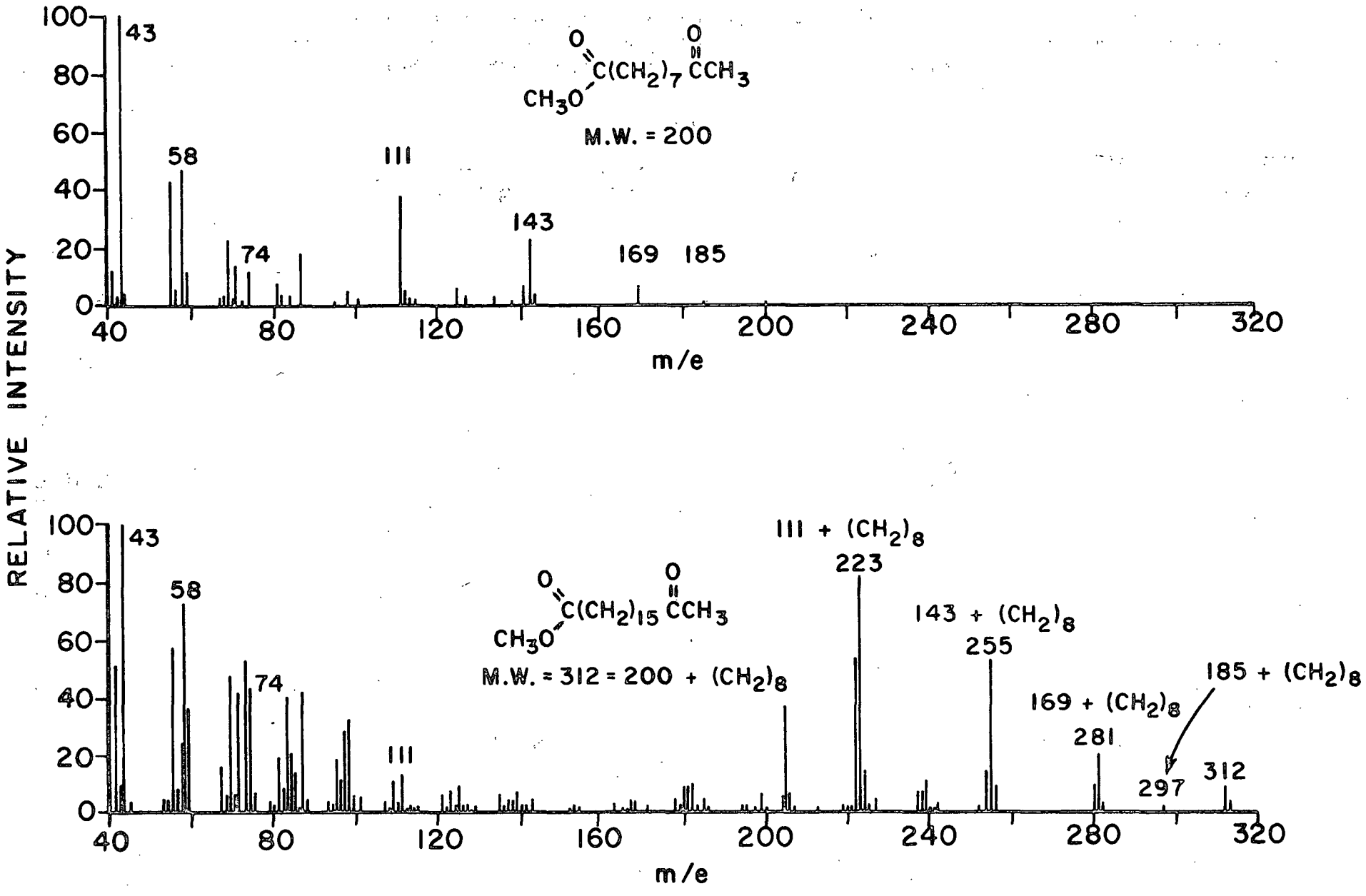


Figure 23. Mass Spectra of ω-Aceto Acid Methyl Esters. Top: Methyl Ester of 9-Oxodecanoic Acid (XXVII, n=7) Recovered in Product of Reaction 2. Bottom: Methyl Ester of 17-Oxooctadecanoic Acid (XXVII, n=15) Published by Ryhage and Stenhagen (68)

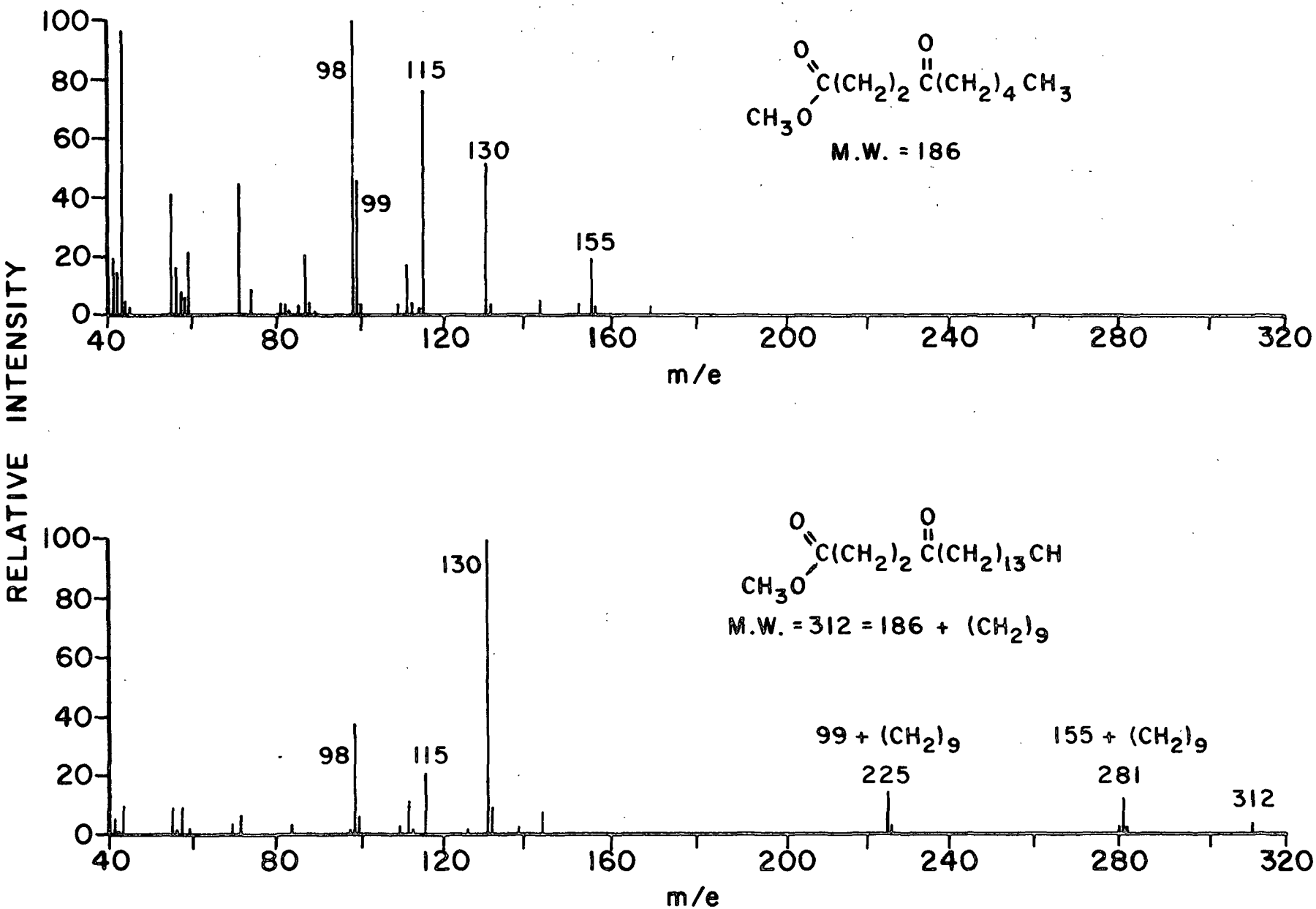
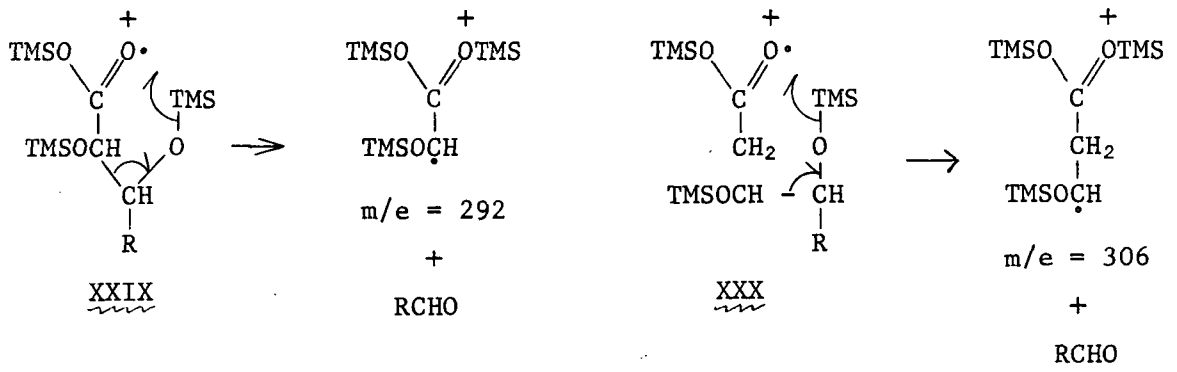


Figure 24. Mass Spectra of γ-Keto Acid Methyl Esters. Top: Methyl Ester of 4-Oxononanoic Acid (XVIII, n=4) Recovered in Product of Reaction 2. Bottom: Methyl Ester of 4-Oxooctadecanoic Acid (XXVIII, n=13) Published by Ryhage and Stenhagen (68)

α,β-DIHYDROXY ACIDS AND β,γ-DIHYDROXY ACIDS

The α,β-dihydroxy acids (XXIX) and β,γ-dihydroxy acids (XXX) were only tentatively identified from the mass spectra of their trimethylsilyl derivatives. No authentic specimen of either type of compound was obtained, and no published spectra were found corresponding to the specific compounds detected. While these compounds represented only minor oxidation products, their possible existence was significant from a mechanistic point of view. The best evidence for the identification of the dihydroxy acids were rearrangement ions possessing mass-to-charge ratios of 292 and 306 for the two respective classes of compounds. Both ions are McLafferty type rearrangement ions formed by migration of a trimethylsilyl group to carbonyl oxygen atoms. Petersson (70) proposed a six-membered ring transition state to account for formation of the 292 ion from α,β-dihydroxy acids and suggested that formation of the 306 ion from β,γ-dihydroxy acids involved a seven-membered ring transition state.



Such rearrangements also occur in long-chain compounds, as shown by Wolff, et al. (71,72). The mass spectra of trimethylsilyl derivatives from 9,10-dihydroxystearic acid (VI) and the trihydroxyoctadecenoic acids (XI) possess peaks of considerable intensity corresponding to ions derived from similar rearrangements.

Mass spectra of all the reaction products identified in this investigation, and mass spectra of the authentic compounds, are tabulated in Appendix VIII. Also presented in the appendix are interpretations of all the mass spectra which were recorded.

POSSIBLE MECHANISMS OF FATTY ACID OXIDATION

HYDROPEROXIDE FORMATION

The initial reactions of fatty acids, fatty acid esters and fatty acid soaps with oxygen in aqueous alkali probably proceed via the classical radical chain mechanism which was summarized by Equations (1)-(6). Carbanions such as those envisioned in Equations (28) and (29) may also contribute to the autoxidation of fatty acid soaps in strong alkali, following the base catalyzed autoxidation scheme outlined earlier in Equations (11)-(20).

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COO^- \xrightarrow{-H^+} \begin{cases} CH_3(CH_2)_6CH{-}CH{-}CH(CH_2)_7COO^- \\ CH_3(CH_2)_7CH{-}CH{-}CH(CH_2)_6COO^- \end{cases} \quad (28)$$

$$CH_3(CH_2)_4CH{=}CHCH\ CH{=}CH(CH_2)_7COO^- \xrightarrow{-H^+} CH_3(CH_2)_4CH{-}CH{-}CH{-}CH{-}CH(CH_2)_7COO^- \quad (29)$$

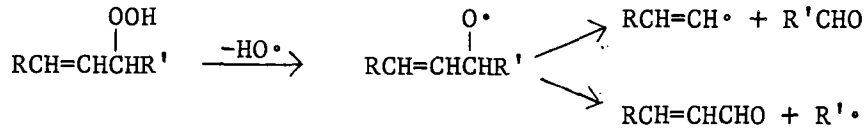
However, no apparent increase in the rate of fatty acid autoxidation is evident at high pH to suggest participation of such carbanions in the autoxidation reactions. In fact, as shown by the results of Reactions 1F-24F, fatty acids and fatty acid esters are oxidized more extensively in systems containing sodium bicarbonate than they are in systems containing only the stronger base, sodium hydroxide. This effect was interpreted as possibly resulting from the formation of carbonate radicals ($\cdot CO_3^-$) as shown previously by Equations (24) and (25).

The carbonate radicals, which would have been formed through reactions between carbonate or bicarbonate ions and hydroxyl radicals, could possibly initiate fatty acid autoxidation by hydrogen atom abstraction. Hydroxyl radicals would also be potential autoxidation initiators, and those highly reactive radicals might have a greater tendency to interact with the substrate. However, the true cause of the enhanced reactivity of fatty acids in bicarbonate-containing systems could not be proven with the data available from this investigation. Regardless of the alkali, hydroperoxides were the expected primary products of fatty acid autoxidation. Probable structures of the postulated hydroperoxides were presented in the Introduction.

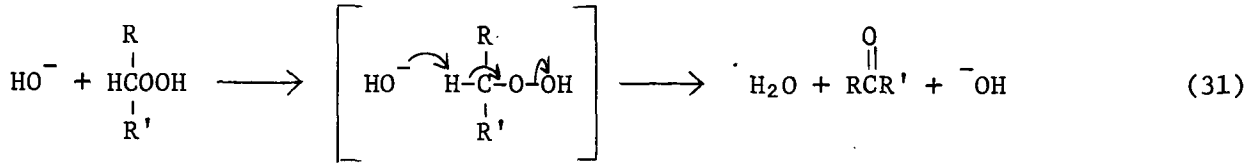
HYDROPEROXIDE DECOMPOSITION

Formation of most oxidation products actually identified can be rationalized on the assumption that hydroperoxides are the initial fatty acid autoxidation products. Since temperatures were relatively high and no attempts were made to exclude transition metal ions from the reaction systems, the hydroperoxides formed were probably very short lived, decomposing rapidly to radicals, alcohols, and carbonyl compounds. The secondary reactions of hydroperoxides are complex and markedly dependent on reaction conditions, particularly temperature and pH. The homolytic decomposition reactions of secondary hydroperoxides have been discussed by Hiatt (73). Hydroperoxides may undergo cleavage reactions leading to formation of alkoxy and peroxy radicals, as was discussed in the Introduction and illustrated by Equations (7)-(10). Such decompositions can be induced thermally, and they are catalyzed by transition metal ions. The alkoxy and peroxy radicals formed can undergo numerous subsequent reactions which yield alcohols and ketones. Hydroperoxides may also decompose homolytically with chain cleavage as shown in Equation (30), and they may undergo a base catalyzed

heterolytic decomposition (73) resulting in the formation of a ketone and water, as shown by Equation (31).



(30)



(31)

The cleavage reaction represented by Equation (30) is commonly observed for cyclic secondary hydroperoxides (73), and it is also a proposed pathway for fatty acid autoxidation (74,75). The free radicals created during such decompositions would be susceptible to further reactions, including autoxidation, yielding hydrocarbons, alcohols, carbonyl compounds and carboxylic acids. The aldehydes and α,β-unsaturated aldehydes formed could also react further. In particular, such compounds are easily oxidized to carboxylic acids.

SECONDARY AUTOXIDATION OF α,β-UNSATURATED KETONES AND ALCOHOLS

Expected decomposition products of fatty acid hydroperoxides include α,β-unsaturated ketones and alcohols. Formation of the ketones should be further promoted by hydroxide according to the reaction shown in Equation (31). Although some of these compounds were identified previously (9,39,40,49), none were detected in this investigation and they were considered to be intermediates in some reaction pathways which led to formation of the identified cleavage products.

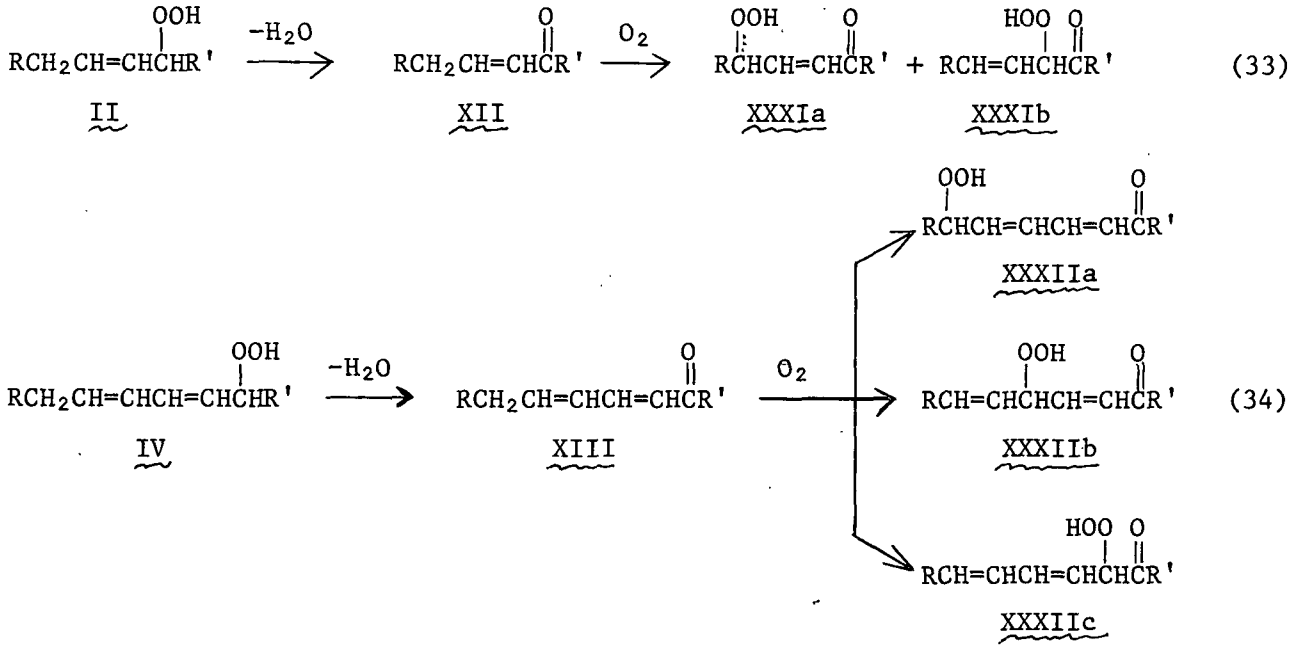
The unsaturated ketones and alcohols are themselves susceptible to further autoxidation. Saturated ketones undergo autoxidation at the carbon atom adjacent to the carbonyl group. Although the reaction may follow a free-radical

pathway (76), it is strongly promoted by base (77). The free-radical reaction obeys the general mechanism outlined in Equations (1)-(6), while the base-catalyzed reaction follows the scheme summarized in Equations (11)-(20). Ketone autoxidation exhibits base catalysis because of the ease with which such compounds form carbanions. α-Hydroperoxy ketones, the primary autoxidation products of saturated ketones, have been isolated and identified after conventional (78) and base catalyzed (79) reactions. The α-hydroperoxy ketones are inherently unstable, decomposing readily to carboxylic acids and aldehydes or ketones as shown by Equation (32). The decomposition occurs in both neutral and alkaline systems.

$$\begin{matrix} HOO\ O \\ |\ \ \| \\ RCHCR' \end{matrix} \longrightarrow RCHO + R'COOH \qquad (32)$$

Under the influence of alkali, α-hydroperoxy ketones can also decompose according to Equation (31), yielding dicarbonyl compounds capable of undergoing base catalyzed rearrangement reactions (80). α,β-Unsaturated ketones are even more susceptible to autoxidation than saturated ketones, since they form free radicals or carbanions which are resonance stabilized by the double bond and the carbonyl group (80). Furthermore, unsaturated ketones can be autoxidized at the saturated carbon atom adjacent to the carbonyl group in some cases (81). α,β-Unsaturated alcohols should also be susceptible to autoxidation. Expected products of such autoxidations include unsaturated α-hydroperoxy alcohols, which can themselves decompose to unsaturated ketones (73).

The probable autoxidation products of α,β-unsaturated keto acids (XII,XIII) derived from oleate hydroperoxides (II) and linoleate hydroperoxides (IV) are shown in Equations (33) and (34), respectively.



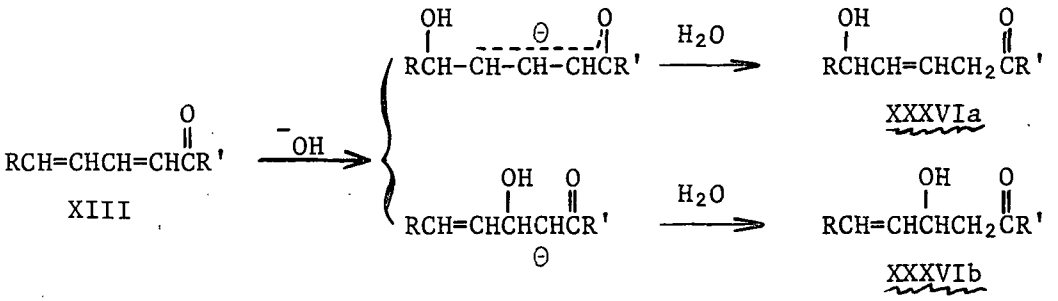
All of the hydroperoxides shown (XXXI,XXXII) are subject to the same decomposition and cleavage reactions which have already been discussed. Furthermore, many of the new decomposition or cleavage products subsequently created, particularly aldehydes, ketones and radicals, could undergo further oxidation. The number of possible secondary autoxidation pathways becomes immense when the reactions of all fatty acid hydroperoxides, and all of their decomposition products, are considered. The reaction pathways will terminate upon formation of saturated acidic products. Those acids can be formed by oxidation of aldehydes or cleavage of hydroperoxy ketones.

BASE CATALYZED REACTIONS OF HYDROPEROXIDE DECOMPOSITION PRODUCTS

In strong alkali, many of the expected hydroperoxide decomposition products are subject to a number of other base promoted reactions in addition to autoxidation. These include Michael additions, reverse Michael additions, reverse aldol condensations, and rearrangements. Such reactions may be enlisted to account for many of the oxidation products identified, although they are not generally

considered in conjunction with fatty acid autoxidation. For example, a scheme-involving sequential Michael addition of water, reverse aldol condensation, base, catalyzed autoxidation, and an intramolecular Cannizzaro reaction can be postulated to rationalize the formation of 2-hydroxynonanedioic acid (XXVI, n=6) and octanedioic acid (XV, n=6) from an α,β-unsaturated keto acid (XIIa) derived from oleic acid. The overall scheme, which is only suggested as a possible reaction pathway accounting for formation of the observed reaction products, is shown in Fig. 25. Analogous reaction sequences can be devised for all of the oleate derived α,β-unsaturated keto acids.

The unsaturated keto acids (XIII) derived from linoleate hydroperoxides should also undergo Michael addition, at either of two sites shown by Equation (35).



(35)

While the 1,6 addition product (XXXVIa) should predominate, significant quantities of the 1,4 addition product (XXXVIb) might also be formed (82).

α,β-Unsaturated alcohols are capable of undergoing base catalyzed rearrangements which result in the formation of saturated ketones (83). Such a reaction involving the 1,6 Michael addition product (XXXVIa) from a linoleate-derived unsaturated keto acid might occur as shown in Equation (36).

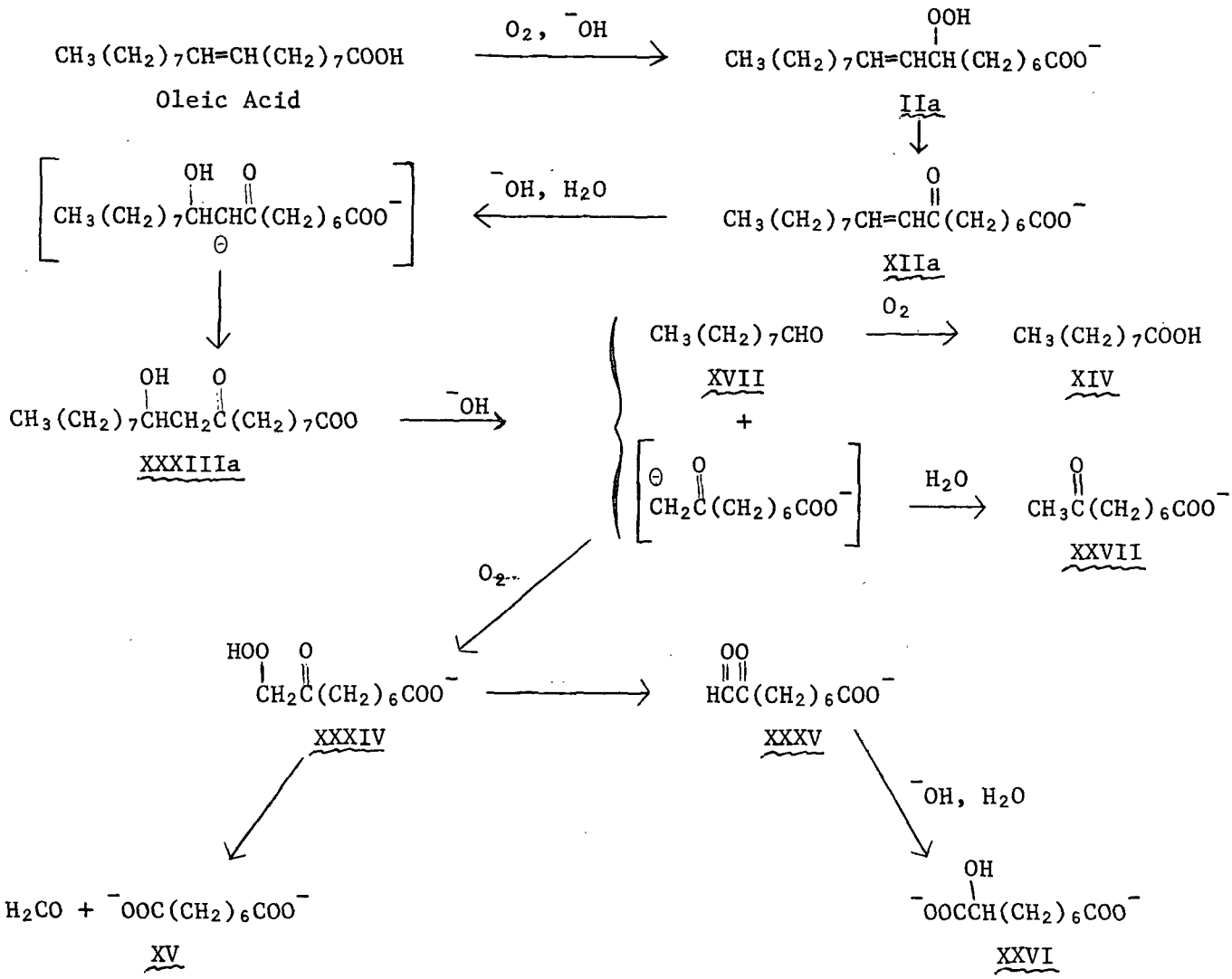
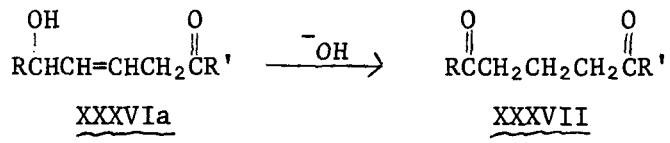


Figure 25. Postulated Scheme for Base Catalyzed Autoxidation of Oleic Acid



(36)

The saturated dicarbonyl product (XXXVII) could undergo a base-catalyzed reverse Michael reaction leading to formation of an α,β-unsaturated ketone (XXXVIII) and a carbanion, as shown in Equation (37).

$$\underset{\text{XXXVIIa}}{RCH_2CH_2CH_2CR'} \xrightarrow{-OH} \underset{\text{XXXVIII}}{RCCH=CH_2} + R'\overset{\Theta}{C}CH_2 + H_2O \qquad (37)$$

The reactions represented by Equations (35)-(37) may be incorporated into an overall scheme which accounts for the formation of 9-oxodecanoic acid (XXVII, n=7) and 2-hydroxydecanedioic acid (XXVI, n=7) from linoleic acid. The scheme, which is outlined in Fig. 26, is similar to that previously developed for oleic acid and illustrated in Fig. 25. Again, the reactions shown in Fig. 26 comprise just one suggested pathway, and analogous schemes can be devised for the other linoleate derived unsaturated keto acids.

Base-catalyzed rearrangements of α,β-unsaturated alcohols (83) can also account for the formation of γ-keto acids (XXVIII), which were fatty acid oxidation products identified during this investigation. Those keto acids could be derived from γ-hydroxy-α,β-unsaturated aldehydes (XXIII) as shown in Equation (38).

$$\underset{\text{XXIII}}{RCHCH=CHCHO} \xrightarrow{-OH} \underset{\text{XXXIX}}{RCCH_2CH_2CHO} \xrightarrow{O_2} \underset{\text{XXVIII}}{RCCH_2CH_2COOH} \qquad (38)$$

The unsaturated hydroxy aldehydes, which have been found among the autoxidation products of methyl linoleate (19,55), could be formed through numerous pathways, one of which is also postulated in Fig. 26.

The intermediate carbanions created during Michael additions, reverse Michael additions,and reverse aldol condensations may also be prone to autoxidation. The hydroperoxides formed would then be susceptible to all the common decomposition and cleavage reactions attributed to hydroperoxides. Some of those reactions might result in formation of α-hydroxy aldehydes (XL), as shown in

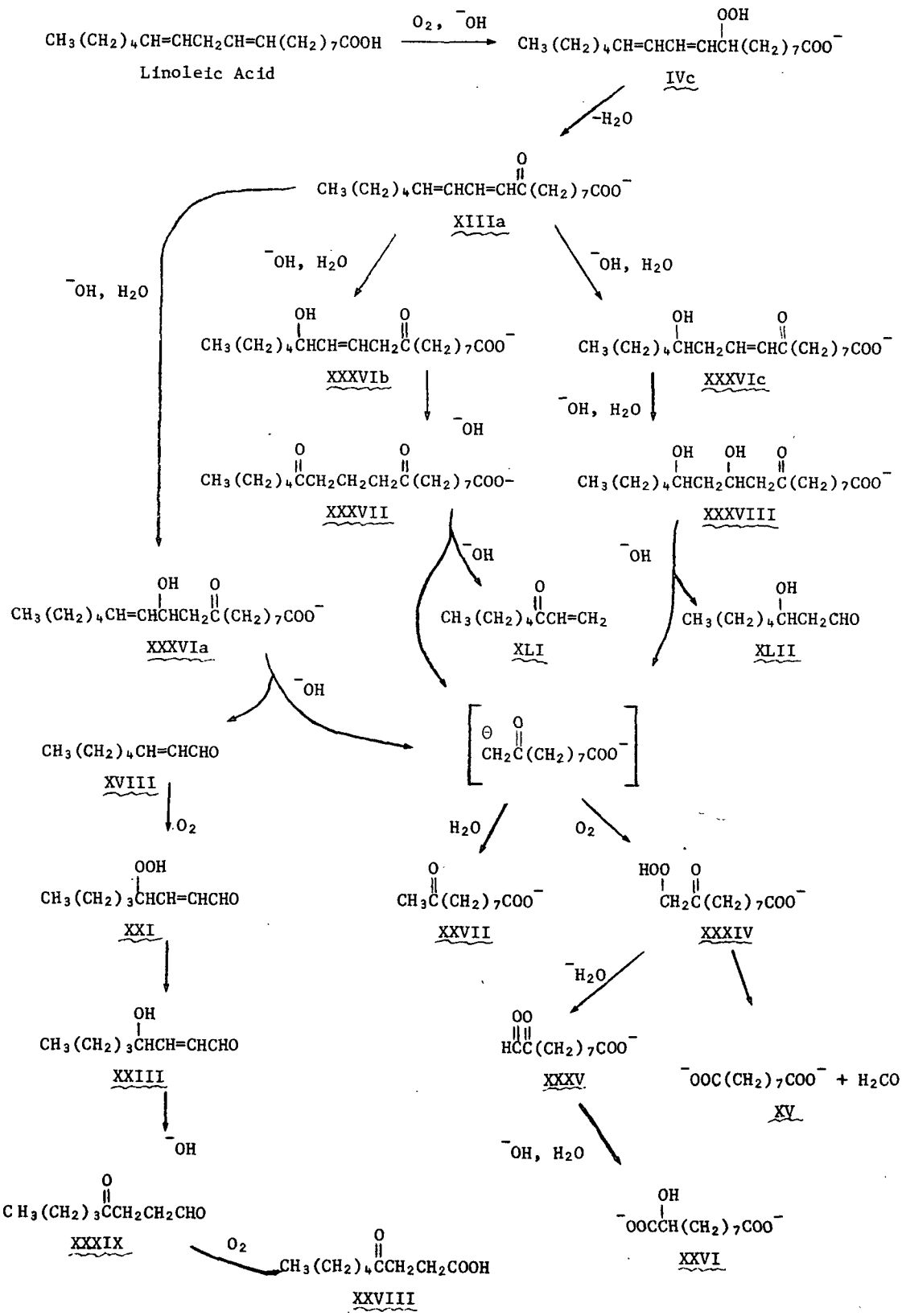
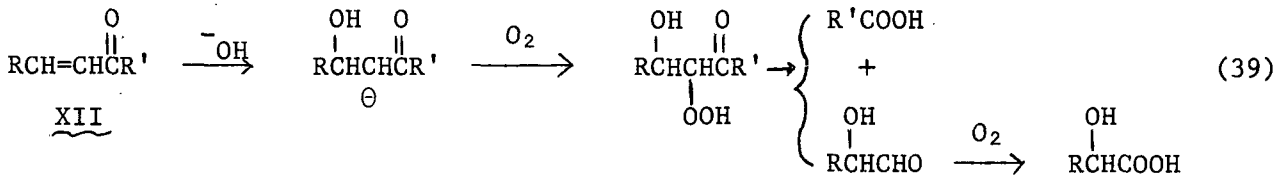
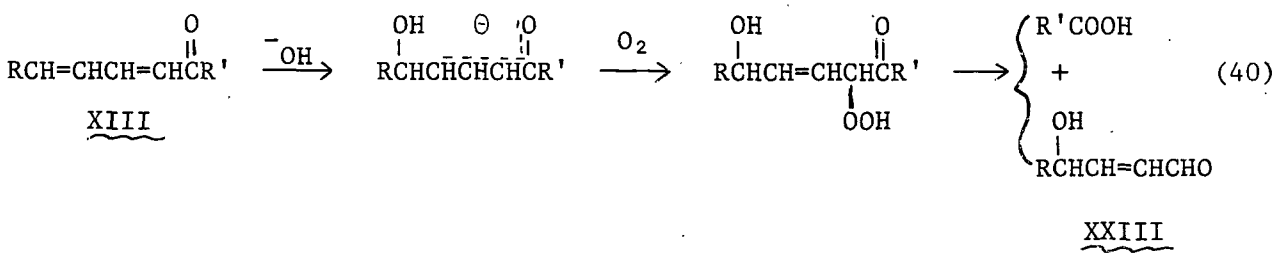


Figure 26. Postulated Scheme for Base Catalyzed Autoxidation for Linoleic Acid

Equation (39). Thus, α-hydroxy aldehydes are other possible precursors of α-hydroxy acids and α-hydroxydicarboxylic acids. A similar reaction which represents an alternate pathway leading to formation of γ-hydroxy-α,β-unsaturated aldehydes (XXIII) is shown in Equation (40).



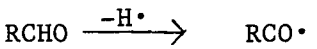
(39)



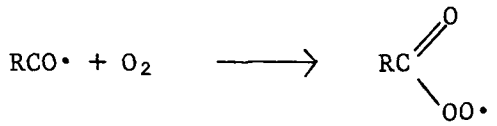
(40)

STEPWISE DEGRADATION OF ALDEHYDES AND ALDEHYDE ACIDS

Saturated aldehydes and aldehyde acids are suspected intermediates in the formation of many of the acidic cleavage products which were identified during this investigation. Compounds of the former type are commonly detected among the autoxidation products of unsaturated fatty acids (49,50,52,57), and aldehyde acids have also been identified (49-51). Aldehydes are very susceptible to oxidation themselves. Normal aldehyde autoxidation (84) follows a radical chain mechanism which is analogous to the basic autoxidation scheme outlined in Equations (1)-(6). The reaction is initiated by abstraction of the aldehydic hydrogen atom, and peroxy acids are the primary autoxidation products, as shown in Equations (41)-(43).



(41)



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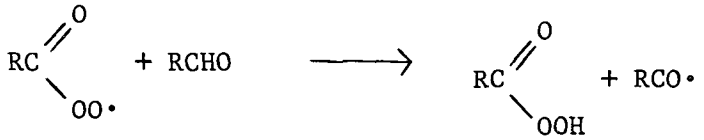
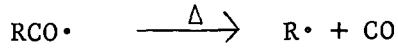


(43)

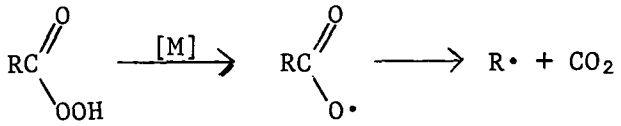
The peroxy acids undergo reactions with other species, including unoxidized aldehydes, to form carboxylic acids, which are usually the terminal products of aldehyde autoxidation.

During aldehyde autoxidation, the radicals formed by Reactions (41) and (43) may follow alternate reaction pathways which do not lead to formation of peroxy acids. When aliphatic aldehydes are autoxidized at temperatures exceeding 100°C, the free radicals initially formed may disproportionate into carbon monoxide and aliphatic free radicals (85), as shown in Equation (44).



(44)

The peroxy acids created during aldehyde autoxidation may also decompose to radicals and carbon dioxide (86), as shown in Equation (45).



(45)

The latter reaction is catalyzed by transition metal ions. The free radicals formed after either reaction may undergo numerous subsequent reactions, including autoxidation. Hydrocarbons, alcohols, aldehydes and carboxylic acids are all potential products of those reactions. Reactions such as those shown in Equations (44) and (45) represent the most probable rationalization for the formation of ω-hydroxy acids (XXIV), which were among the prominent products identified during this study. No ω-hydroxy acids containing more than eight

carbon atoms were detected, so they were not formed by direct cleavage of fatty acid molecules at the locations of their double bonds. However, the eight carbon ω-hydroxy acid, 8-hydroxyoctanoic acid (XXIV, n=6) could be formed by decomposition of 9-oxononanoic acid (XVI, n=7) according to Reaction (44) or (45). Formation of the latter compound can occur through several pathways, including the direct homolytic cleavage of hydroperoxides shown previously by Equation (30).

Under strongly alkaline conditions aldehydes, like ketones, are susceptible to autoxidation at the α-carbon atom (80), as shown in Equation (46).

$$\underset{\text{XVII}}{RCH_2CHO} \xrightarrow{-H^+} R\bar{C}H\bar{C}HO \xrightarrow{O_2} \underset{\text{XLII}}{RCH(OOH)CHO} \qquad (46)$$

The presumed primary products of base-catalyzed aldehyde autoxidation are α-hydroperoxy aldehydes (XLII), and they may undergo further reactions which yield lower aldehydes (XVII), carboxylic acids (XIV) and α-keto aldehydes (XX), as shown in Equation (47).

$$\underset{\text{XLII}}{RCH(OOH)CHO} \rightarrow \underset{\text{XVII}}{HCOOH + RCHO} \xrightarrow{O_2} \underset{\text{XIV}}{RCOOH} \qquad (47)$$

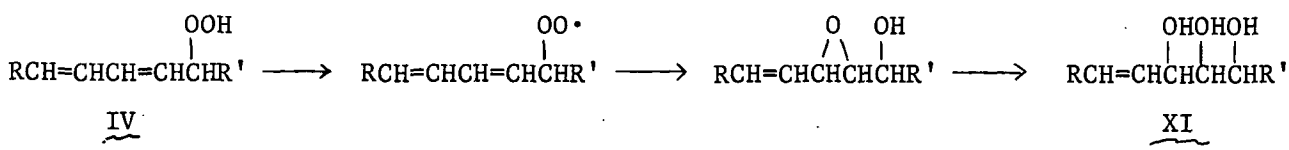
$$\underset{\text{XLII}}{RCH(OOH)CHO} \xrightarrow{-OH} \underset{\text{XX}}{RCC(=O)CH(=O)} \xrightarrow{-OH,\ H_2O} \underset{\text{XXV}}{RCH(OH)COOH}$$

The latter compounds can undergo an intramolecular Cannizzaro reaction to yield α-hydroxy acids (XXV), and the aldehydes can undergo further degradation to products of even lower molecular weight. Reactions (46) and (47) should be

equally applicable to aldehyde acids. Aldehydes and aldehyde acids are thus capable of undergoing thermally induced or base-catalyzed reactions which result in the formation of products containing one less carbon atom than the original compound. Included among those products are lower aldehydes. Thus, such compounds may be involved in a "peeling" type reaction which eventually results in complete oxidation of the original molecule. Such reactions may account in part for the enhanced formation of low molecular weight products observed at high temperatures.

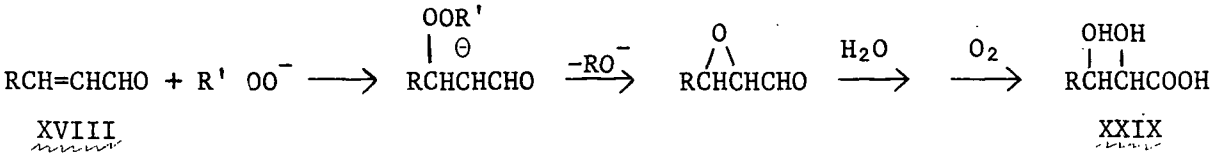
FORMATION OF POLYHYDROXY COMPOUNDS

Formation of 9,10-dihydroxystearic acid and the trihydroxyoctadecenoic acids probably results from reactions between unoxidized fatty acid molecules and various intermediate species present in the reaction system. Peroxy radicals and peroxy acids react with olefins to yield epoxides, and upon hydrolysis the epoxides yield dihydroxy compounds. The mechanism of the reaction between peroxy radicals and olefins was discussed in the Introduction and has been described previously (32). Intramolecular epoxidation has also been proposed as a reaction of fatty acid hydroperoxides. Formation of the trihydroxyoctadecenoic acids (XI) from linoleate hydroperoxides (IV) might occur as a result of such reactions (44).



The α,β-dihydroxy acids (XXIX) which were tentatively identified among the oxidation products of methyl linoleate are possible products of reactions between peroxy radicals and α,β-unsaturated aldehydes (XVIII). Furthermore, in strongly alkaline systems, peroxy anions ($R'OO^-$) may undergo Michael additions

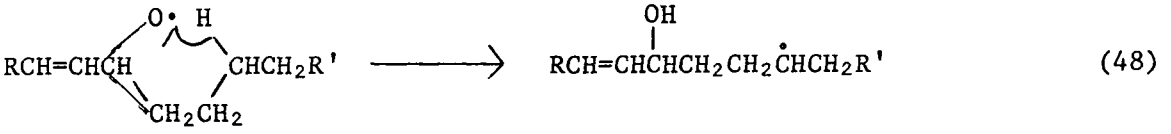
with α,β-unsaturated carbonyl compounds (87). The possible formation of an α,β-dihydroxy acid from such a reaction is illustrated below:



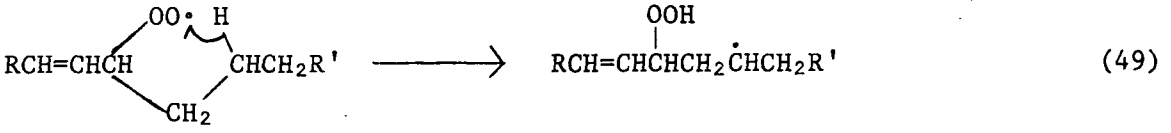
XVIII XXIX

OTHER POSSIBLE OXIDATION PATHWAYS

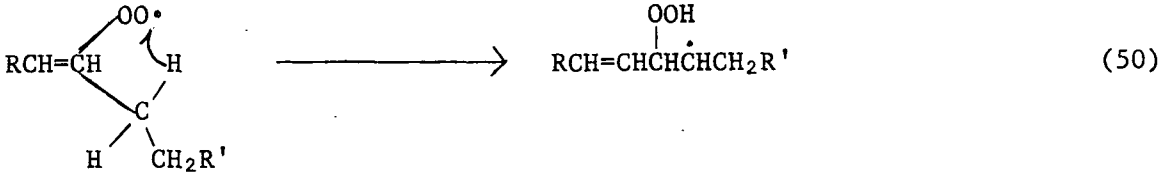
Other reactions which may explain the random nature of fatty acid autoxidation include intramolecular hydrogen atom abstraction and alkali-induced double bond migrations. A reaction of the former type would promote secondary autoxidation of oxidized fatty acid molecules at different sites on the carbon atom chain, while the latter reaction would relocate the site of initial attack by oxygen. Intramolecular hydrogen abstractions might be expected to occur after homolytic decomposition of the hydroperoxide primary products to alkoxy and peroxy radicals. Hydrogen atom abstractions involving five- or six-membered ring transition states, as envisioned in Equations (48)-(50), would create new sites for autoxidation away from the locations of the double bonds.



(48)



(49)



(50)

Strong alkali and high temperatures can induce isomerization and migration of the double bonds in unsaturated fatty acids. Linoleic acid, which contains two methylene-interrupted double bonds, is partially converted to its conjugated isomers during kraft pulping (5) or simple alkaline hydrolysis (88). Furthermore, oleic acid and linoleic acid are oxidized to saturated fatty acids containing two and four less carbon atoms, respectively, by the action of fused potassium hydroxide (89).

CONCLUSIONS

The reactions of fatty acids and fatty acid esters with oxygen and alkali follow a pattern which is the opposite of that observed for similar reactions involving carbohydrates and lignin. While oxidations of those materials are promoted by sodium hydroxide, fatty acids and their esters undergo much more extensive degradation in the presence of sodium bicarbonate. This effect may be due in part to the catalysis of fatty acid autoxidation by carbonate radicals derived from the alkali. The enhanced degradation of fatty acid derivatives by oxygen in bicarbonate systems has serious implications with respect to tall oil recovery from an oxygen-alkali delignification process. If bicarbonate or carbonate is the alkali employed, then extensive oxidation of the tall oil fatty acid components may be anticipated. Furthermore, the fatty acids in wood exist predominately as triglycerides, and the weaker alkalis (carbonate and bicarbonate) will not effect appreciable saponification of those esters. Thus, any esters which survive the oxygen treatment will not be recovered by conventional pulp washing. Because of these factors, recovery of tall oil fatty acids from a bicarbonate- or carbonate-based delignification process may not be possible without some type of pretreatment designed to remove those compounds. On the other hand, since the fatty acids are more stable in the presence of hydroxide, and since the esters are saponified by the stronger alkali, recovery of tall oil fatty acids during oxygen-hydroxide delignification will be feasible. Some losses due to oxidation will always occur, but appreciable fatty acid yields can be anticipated in the presence of hydroxide unless very severe reaction conditions are imposed. The saturated acids should undergo very limited oxidation, and degradation of oleic acid will be less extensive than that of linoleic acid.

Fatty acid oxidation is increased to about the same extent if the temperature is raised from 100 to 160°C, or if the reaction time is extended from 2 to

8 hr. However, the effect of either of those variables is much less than that which is observed when the alkali is changed from sodium hydroxide to an equimolar amount of sodium bicarbonate.

Wood appears to exert a protective effect with respect to fatty acid autoxidation. The protective effect may result from limitations imposed by oxygen diffusion, or it may reflect the antioxidant characteristics of phenolic compounds derived from the lignin in wood. In the presence of hydroxide, the protective effect of wood is apparently offset by the pH drop which results from the reactions of lignin with oxygen and the alkali. Furthermore, the phenols may not be effective antioxidants when ionized. Thus, a high lignin content is beneficial in terms of tall oil retention in systems containing bicarbonate, but indirectly harmful in the presence of hydroxide.

The nature of the substrate influences the effect of oxygen pressure. In systems containing only cotton, which may be considered a model for delignified wood, little or no increase in the extent of fatty acid oxidation is achieved when the oxygen pressure is increased from 690 to 3500 kPa. However, if wood is present, fatty acid degradation increases significantly when the oxygen pressure is increased.

When the tall oil fatty acids are degraded by oxygen and alkali, complex mixtures of reaction products are created. Many of the oxidation products formed, including dicarboxylic acids and hydroxy acids, are themselves commercially valuable, but their recovery is probably infeasible. Because the reactions are not selective, the oxidation products are generally produced in very low yields, and they are not easily isolated from the product mixtures. The oxidation reactions are more selective at 100°C than at 130 or 160°C, but yields of individual compounds are low even at the low temperature.

The primary products of all fatty acid autoxidations are presumably hydroperoxides, although epoxy and hydroxy compounds may result from reactions between unsaturated fatty acids and peroxides. Decomposition reactions of the hydroperoxides appear to be profoundly dependent on reaction conditions. The hydroperoxides may cleave homolytically to aldehydes, aldehyde acids and radicals. Such compounds, particularly the aldehydes and aldehyde acids, are themselves easily oxidized further to mono- and dibasic carboxylic acids. The hydroperoxides also decompose to noncleavage products, of which α,β-unsaturated keto acids or esters are thought to be the most significant. Those compounds, whose formation may be promoted by base, can be autoxidized themselves. They may also undergo base catalyzed reactions which involve addition of water and cleavage. Such reactions may account for formation of α-hydroxy acids and α-hydroxy dicarboxylic acids, which are major products of fatty acid autoxidations conducted in strong aqueous alkali.

Many low molecular weight reaction products are formed during the fatty acid oxidations, and the concentrations of such compounds increase at elevated temperatures. Many of the identified oxidation products, particularly the dicarboxylic acids, are not themselves easily autoxidized, and are not likely to represent precursors of the low molecular weight compounds. Formation of those compounds may result in part from the stepwise decarbonylation of aldehydes and aldehyde acids, which are thought to be precursors of the acidic oxidation products. High temperatures promote the degradation of aldehydes to hydrocarbons, alcohols, carbonyl compounds and acids. The random nature of autoxidation also suggests some type of autocatalysis, such as intramolecular hydrogen atom abstraction, which accelerates the degradation of unsaturated fatty acids and their hydroperoxides.

SUGGESTIONS FOR FUTURE WORK

Included among the results of this thesis are several phenomena which invite further investigation. Listed below are some topics which might be considered as bases for future work. In each of those follow-up studies, analysis of the complex oxidation reactions could be simplified by conducting them with pure compounds in aqueous solutions. Employing such a system might permit kinetic treatment of the data obtained, and it would allow measurement of hydroperoxide concentrations.

1. The Effect of Carbonate and Bicarbonate on the Autoxidation of Unsaturated Fatty Acids

When autoxidized in an aqueous system containing a wood meal or cotton substrate, unsaturated fatty acids and their esters undergo much more extensive degradation in the presence of sodium bicarbonate than in the presence of sodium hydroxide. However, the exact cause of this phenomenon could not be ascertained from the data obtained during the present study. The nature of the bicarbonate-promoted reaction might be more clearly understood if the reactions of oxygen with aqueous alkaline solutions of pure fatty acids were examined in greater detail. The experimental program should be designed to determine whether the autoxidation reactions are more influenced by the pH of the solution, or by the actual concentration of carbonate or bicarbonate. Detection of carbonate radicals might also be attempted, possibly using the spectrophotometric technique employed by Behar, et al. (67).

2. The Mechanism of Fatty Acid Autoxidation in Aqueous Sodium Hydroxide

The rate of fatty acid autoxidation was not accelerated by sodium hydroxide in the aqueous systems examined. However, the secondary reactions of the oxidized fatty acids were profoundly affected by strong alkali, as evidenced by the

enhanced formation of α-hydroxy mono- and dibasic carboxylic acids. While some pathways were proposed to account for formation of those compounds, the actual mechanisms of the base-promoted reactions were not proven. Further work in this area could deal with the base catalyzed reactions of suitable fatty acid derivatives or intermediate oxidation products. Such compounds would include fatty acid hydroperoxides (II,IV), α,β-unsaturated keto fatty acids (XII,XIII) and saturated aldehyde acids (XVI). These investigations should include comparisons of reactions conducted in oxygen-free and oxygen-enriched sodium hydroxide solutions.

3. Changes in the Mechanism of Fatty Acid Autoxidation Induced by Changes in the Reaction Temperature

An increase in reaction temperature exerted a pronounced effect on the distribution of secondary oxidation products during fatty acid autoxidation. This effect was thought to result from the stepwise decarbonylation of aldehydes and aldehyde acids formed during the autoxidation reactions. To check this hypothesis, the formation of those aldehydic compounds would have to first be proven. If they are indeed created during autoxidation of fatty acids in aqueous alkali, then the reactions of the aldehyde acids (XVI) should be examined independently in both hydroxide- and bicarbonate-containing systems at varying temperatures. The primary intent of the investigation would be proof of the decarbonylation reaction and the possibility of its stepwise character. However, competing reactions such as those proposed in Equations (46) and (47) should also be considered for reactions carried out in the stronger alkali.

4. Possible Antioxidation by Lignin Derived Phenolic Compounds

Fatty acid autoxidation is apparently retarded by the lignin in wood, particularly in bicarbonate-containing systems. The inhibition of fatty acid autoxidation by phenols has already been extensively investigated. However, no

consideration has been given to the possible occurrence of such a phenomenon in aqueous alkaline solutions. To test the hypothesis of antioxidation by lignin, a study could be undertaken to determine the effect of added lignin model compounds on the autoxidation of fatty acids in aqueous alkali. Particular attention should be directed toward the effect of pH to determine if the suspected antioxidant properties are lost when the phenols are ionized.

While each of the investigations proposed would involve a simplified reaction system containing aqueous alkaline solutions of fatty acid soaps, the possible effect of substrate on fatty acid autoxidation should always be considered as well, particularly if the results are not consistent with those found during the present study. The participation of substrate might be further examined by including suitable carbohydrate model compounds, either saccharides or anhydro alditols, in some reaction systems. Such compounds might influence the course of fatty acid autoxidation as a result of their own reactions with oxygen and alkali.

In any additional investigations of fatty acid autoxidation in aqueous alkaline systems, attempts could be made to achieve a more complete material balance than was obtained during the present study. In particular, efforts should be made to determine if the bulk of matter consumed during reactions with oxygen and alkali can be accounted for by the formation of carbon dioxide, formic acid, glycolic acid, lactic acid, and other low molecular weight products. Conversely, the possible formation of volatile or neutral compounds and polymers might also be investigated. Unfortunately, the complexity of the reactions makes any complete analysis of reaction products very difficult.

EXPERIMENTAL

GENERAL ANALYTICAL PROCEDURES

Melting points were measured on a Thomas Hoover capillary melting point apparatus.

Infrared spectra were recorded on a Perkin Elmer 700 spectrophotometer. The spectra of liquids were taken from neat films on sodium chloride plates, while the spectra of solids were taken from potassium bromide pellets.

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL FX-100 Fourier transform NMR spectrometer using tetramethylsilane as internal standard. Samples were dissolved in deuterated acetone.

Thin-layer chromatography was carried out on microscope slides coated with Silica Gel G (Brinkman Instruments, Inc.). Compounds were visualized with 4:1 methanol-sulfuric acid (v/v) or with vanillin-sulfuric acid reagent (90). Column chromatography was carried out on Silica Gel 60 (Brinkman Instruments, Inc.). The fractions were collected on a Gilson volumetric fraction collector.

Gas-liquid chromatography of fatty acid esters and fatty acid oxidation products was carried out with two different instruments. One was a Varian Aerograph 1200 gas chromatograph equipped with a hydrogen flame ionization detector and a Honeywell Electronic 16 recorder with a Disc integrator. The carrier gas was prepurified nitrogen (Matheson Gas Products). The other instrument was a Perkin Elmer 3920 dual column gas chromatograph equipped with a hydrogen flame ionization detector and a Perkin Elmer 56 recorder with a Disc integrator. The carrier gas was prepurified helium (Matheson Gas Products). Descriptions of the gas chromatographic columns and operating conditions employed with both instruments are provided in Appendix VI.

Gas analyses were carried out on a Varian Aerograph 200 dual column gas chromatograph equipped with a thermal conductivity detector and a Honeywell Electronic recorder with a Disc integrator. Descriptions of the column and operating conditions are given in Appendix V.

Mass spectra were obtained from a Du Pont 21-491 mass spectrometer interfaced via a jet separator with a Varian Aerograph 1400 gas chromatograph equipped with a hydrogen flame ionization detector and a Hewlett-Packard 7128A recorder. The mass spectra were recorded on a Century GPO 460 recorder. The carrier gas was ultra high purity helium (minimum purity 99.999%, Matheson Gas Products). Compounds were analyzed as their methyl esters, methyl ester-trimethylsilyl ethers or trimethylsilyl derivatives both with and without added perfluorotributyl amine internal standard. Descriptions of the gas chromatographic columns and operating conditions employed during the mass spectral analyses are provided in Appendix VIII. The mass spectra and their interpretations are tabulated in Appendix VIII.

MATERIALS AND REACTANTS

FATTY ACIDS AND FATTY ACID ESTERS

Commercial grade palmitic acid, oleic acid and linoleic acid were obtained from Emery Industries and Ashland Chemicals Co. Stearic acid was obtained from Eastman Chemicals. The acids were converted to their methyl esters in excess acidified methanol (91). The unsaturated esters were prepurified by crystallization of urea inclusion complexes (91), and all the esters were further purified by distillation under reduced pressure. The distillates thus obtained represented the starting materials used in Reactions 1-3, 7, 8, 11 and 12. The methyl esters were first saponified in 0.5N ethanolic potassium hydroxide (91) for Reactions 1, 2, 11 and 12. Methyl docosanoate (99%) purchased from Analabs, Inc. and methyl

eicosanoate (99%) purchased from Applied Science Laboratories, Inc. were used as received in Reactions 7 and 8. Methyl oleate or oleic acid (both 99%) purchased from U.S. Biochemicals Corp. was used in Reactions 4, 9 and 22F-24F. The methyl oleate used in Reactions 1F-21F, also purchased from U.S. Biochemical Corp. and allegedly 99% pure, actually consisted of 86% methyl oleate, 6% methyl linoleate and 8% unidentified fatty acid esters.

Pure methyl linoleate was prepared from safflower oil. The oil was saponified in 1N methanolic potassium hydroxide, and saturated acids were removed by crystallization of their urea inclusion complexes (91). Tetrabromostearic acid was prepared from the fraction enriched in unsaturated acids by the procedure of McCutcheon (92), and after debromination in zinc-methanol the methyl linoleate recovered was distilled to yield a product of 99% purity. This material was used in Reactions 5, 6, 10 and 1F-24F.

The fatty acid contents of all starting materials and reaction products were determined by gas-liquid chromatography. Methyl stearate and methyl palmitate, both purified by repeated distillation, were sometimes used as internal standard. Eicosanoic acid (99%) purchased from U.S. Biochemical Corp. was the internal standard used in conjunction with Reactions 9-12 and 1F-24F.

FATTY ACID OXIDATION PRODUCTS

Dimethylnonanedioate, dimethyloctanedioate and dimethylheptanedioate were purchased from Analabs, Inc. Additional dimethylheptanedioate, which was hydrolyzed to yield heptanedioic acid, was obtained from Eastman Chemicals, and succinic acid was supplied by Merck and Co. Octanedioic acid and decanedioic acid were purchased from U.S. Biochemical Corp. The latter compound was used as internal standard during gas chromatographic analyses of fatty acid oxidation products. 2-Hydroxybutyric acid, 2-hydroxypentanoic acid, 2-hydroxyhexanoic

acid, 2-hydroxyoctanoic acid, 2-hydroxypentanedioic acid and malic acid were all purchased from Tridom Chemicals, Inc. Nonanoic acid was obtained from Aldrich Chemical Co.

9,10-Dihydroxystearic Acid

The low melting isomer of 9,10-dihydroxystearic acid was prepared from oleic acid by oxidation with performic acid as described by Swern and Scanlan (93). The high-melting isomer of 9,10-dihydroxystearic acid was prepared from oleic acid by oxidation with alkaline potassium permanganate as outlined by Robinson and Robinson (94).

9-Oxononanoic Acid and Nonaldehyde

9,10-Dihydroxystearic acid was oxidized with periodic acid as described by King (95). The product was steam distilled; nonaldehyde was recovered in the distillate and 9-oxononanoic acid remained in the nonvolatile fraction. Neither product was further purified, but both were used in subsequent syntheses.

2-Hydroxydecanedioic Acid

The nonsteam volatile product from the periodic acid oxidation of 48 g of 9,10-dihydroxystearic acid was mixed with 18 g sodium cyanide and 35 mL concentrated hydrochloric acid in 100 mL water. The temperature of the mixture was maintained at or below 15°C with stirring for 2 hr. Concentrated hydrochloric acid (110 mL) was then added, and the mixture was heated on a steam bath for several hours. Upon cooling a white solid precipitated, which, after three recrystallizations from hot water, yielded 9.2 g of 2-hydroxydecanedioic acid melting at 119-120°C; literature: m.p. 116°C (96). The acid was treated with diazomethane, and infrared and proton NMR spectra were recorded of the free acid and dimethyl ester. The NMR spectra are discussed in Appendix VII. Mass spectra of the dimethyl ester, dimethyl ester-trimethylsilyl ether and trimethylsilyl ester-ether are tabulated in Appendix VIII.

9-Hydroxynonanoic Acid

The nonsteam volatile product from the periodic acid oxidation of 26 g of 9,10-dihydroxystearic acid was dissolved in 200 mL 5% sodium carbonate. Sodium borohydride (5 g) was added, and the solution was left overnight. The product was acidified and extracted with ether. The ether extract was dissolved in a slight excess of dilute potassium hydroxide and extracted with ether to remove neutrals. The aqueous phase was then evaporated to dryness, and the salts were dissolved in 100 mL hot absolute ethanol. The solution was cooled, and the recrystallized salts were recovered by filtration, acidified and extracted with ether. After the ether had been dried and distilled off, the product was dissolved in hot ethyl acetate and cooled in dry ice-acetone. 9-Hydroxynonanoic acid (2.6 g) melting at 45-50°C was recovered; literature: m.p. 53-54°C (97). Some of the acid was methylated with diazomethane. Proton NMR spectra of both the free acid and methyl ester were recorded. The spectra are discussed in Appendix VII. Mass spectra of the methyl ester, methyl ester-trimethylsilyl ether and trimethylsilyl ester-ether were also recorded. The latter spectrum is tabulated in Appendix VIII.

Nonanedioic Acid

The nonsteam volatile product from the periodic acid oxidation of 26 g of 9,10-dihydroxystearic acid was mixed with 20 mL concentrated sulfuric acid in 130 mL water. The mixture was cooled to 15°C, and 20 g potassium permanganate were slowly added such that the temperature remained below 20°C. After standing overnight the product was made alkaline with sodium hydroxide, heated on a steam bath and filtered. The hot filtrate was acidified, treated with decolorizing carbon and filtered through celite on a steam heated Buchner funnel. The filtrate was concentrated to a volume of 500 mL, heated until the solution was clear, and cooled to room temperature. The material which precipitated was

recrystallized once from 400 mL hot water, yielding nonanedioic acid (5.5 g) melting at 105-106°C; literature: m.p. 106.5°C (98). The mass spectrum of the ditrimethylsilyl ester of this compound was recorded and is tabulated in Appendix VIII.

2-Hydroxydecanoic Acid

The steam distillate from the periodic acid oxidation of 48 g of 9,10-dihydroxystearic acid was mixed with 10 g sodium bisulfite in 28 mL water. 2-Hydroxydecanoic acid was prepared from the bisulfite addition compound according to the procedure described by Fieser (99) for the preparation of mandelic acid. Some difficulty was encountered in purifying the product, but eventually 3.5 g of 2-hydroxydecanoic acid melting at 67-69°C was recovered; literature: m.p. 70.5°C (100). Some of the acid was treated with diazomethane. Infrared and proton NMR spectra of the free acid and methyl ester were recorded. The NMR spectra are discussed in Appendix VII. Mass spectra of the methyl ester, methyl ester-trimethylsilyl ether and trimethylsilyl ester-ether were also recorded. The latter spectrum is tabulated in Appendix VIII.

Hexanedioic Acid

Hexanedioic acid was prepared by oxidation of cyclohexanone with potassium permanganate as described by Fieser (99).

WOOD MEAL AND COTTON LINTERS

Loblolly pinewood chips were ground in a Wiley mill to pass through a plate with 1/8 inch perforations. The wood meal was extracted for 8 hr with acetone in a Soxhlet extractor and air dried. The wood meal was leached in water saturated with sulfur dioxide, washed thoroughly with distilled water and air dried again. The metal ion contents of the wood, measured before and after the acid wash, were determined and are reported in Appendix IX.

Cotton linters pulp was received from Dr. N. S. Thompson. The cotton was air dried and used as received. The metal ion content of the cotton, reported in Appendix IX, was measured.

METHANOLIC HYDROCHLORIC ACID

Five percent methanolic hydrochloric acid, sometimes used to esterify fatty acids or their oxidation products, was prepared by passing hydrogen chloride (Matheson Gas Products) through dry methanol until the desired weight gain was achieved.

DIAZOMETHANE

Diazald (N-methyl-N-nitroso-p-toluenesulfonamide) was purchased from Aldrich Chemical Co. Ether solutions of diazomethane were prepared from that compound following the procedure recommended by Aldrich.

REAGENTS

Sodium hydroxide, sodium carbonate, sodium bicarbonate, and all chemicals not otherwise mentioned were obtained from suppliers as reagent grade chemicals and used as received.

WATER

Simply distilled water was used in all oxidations of fatty acids and fatty acid esters. The water used in Reactions 1F-24F was obtained from a common source and stored in a clean glass bottle.

OXIDATIONS OF FATTY ACID SOAP SOLUTIONS

The initial oxidations of fatty acid soaps (Reactions 1 and 2) were conducted in the stirred, Teflon-lined reactor described by Sinkey (101). The fatty acids were dissolved in 200 mL 0.3N sodium hydroxide and preheated to 120°C in the

reactor. The vessel was then pressurized to 970 kPa with oxygen. After the desired reaction time, the reactor was cooled with cold water and vented to atmospheric pressure.

The last two soap oxidations (Reactions 11 and 12) were carried out in the stainless steel reactor used during oxidations of fatty acid methyl esters and described in Appendix II. For the latter two reactions, the soaps were dissolved in 100 mL 2N sodium hydroxide and sealed in the reaction vessel, which was immediately pressurized to 3500 kPa with oxygen. The reactor was then lowered into an oil bath preheated to 160°C. After the desired reaction time the vessel was cooled in ice water and vented.

The products of Reactions 1 and 2 were extracted with organic solvents and analyzed by gas-liquid chromatography as their methyl esters. The products of Reactions 11 and 12 were freeze dried and analyzed as their trimethylsilyl derivatives. More detailed descriptions of the analytical procedures employed after the fatty acid soap oxidations are provided in Appendix I.

OXIDATIONS OF FATTY ACID METHYL ESTERS

Oxidations of fatty acid methyl esters were performed in a 1-liter stainless steel Parr bomb, which is described in more detail in Appendix II. The methyl esters were dissolved in acetone and mixed thoroughly with the wood meal (50 g) or cotton linters (30 g) substrate. The acetone was driven off by evaporation under reduced pressure at 40°C until the odor of the solvent could not be detected. Prior to each reaction, the lower part of the reaction vessel, containing 175 mL water, was preheated to 80°C on a hot water bath. The alkali (11 g sodium hydroxide, 14.6 g sodium carbonate or 23.1 g sodium bicarbonate) was dissolved in the hot water, and this solution was mixed thoroughly with the ester-impregnated substrate. The quantities of wood meal or cotton linters were

sufficient to absorb essentially all of the aqueous solutions of alkali, leaving a porous mat of substrate, alkali and fatty acid ester. Immediately after the reactants were mixed, the reaction vessel was sealed and purged with oxygen; the sealed reactor was pressurized to 690 kPa with oxygen and vented three times in succession. The reactor was then pressurized with oxygen to the desired nominal pressure and immediately lowered into an oil bath which had been preheated to the desired reaction temperature. Measurement of the reaction time commenced at that point. Upon completion of each reaction, the reactor was cooled in ice water and vented to atmospheric pressure. The reaction products were either washed from the substrate as their salts, or acidified and extracted with solvents. The reactants and products recovered were analyzed by gas-liquid chromatography as their methyl esters or trimethylsilyl derivatives. More detailed descriptions of the analytical procedures employed for all reactions are provided in Appendix III.

OXIDATIONS OF FATTY ACID OXIDATION PRODUCTS

Six supplementary oxidations of selected fatty acid oxidation products were carried out in the same reactor used during the oxidations of fatty acid methyl esters. All reactions were conducted with cotton linters (30 g), and the procedure just described for oxidation of fatty acid methyl esters was followed. However, the reactants were not first impregnated onto the substrate. Instead, the compounds were dissolved in the aqueous alkali and mixed with the substrate just prior to oxidation. Nonanedioic acid underwent reaction twice, once with sodium hydroxide (11 g) and once with sodium bicarbonate (23.1 g). Similarly, two mixtures consisting of 2-hydroxydecanoic acid and 2-hydroxydecanedioic acid, and two other mixtures, each of which contained both the low melting and high melting isomers of 9,10-dihydroxystearic acid, were subjected to oxidation in the presence of both hydroxide and bicarbonate. The alkaline reaction products

were washed from the substrate with water. The washings were acidified and extracted with ether. The products recovered were analyzed by gas-liquid chromatography as their trimethylsilyl derivatives. The results of those product analyses are summarized in Appendix IV.

OXIDATION OF FATTY ACID ESTERS: MEASUREMENT OF TEMPERATURE ISOTHERMS AND GAS ANALYSES

Three supplementary oxidations of fatty acid methyl esters were carried out in the presence of substrate and alkali using a reaction vessel essentially identical to the reactor utilized during the previous oxidations of fatty acid esters. The experimental procedures followed were also the same as those employed previously. However, the reactor was equipped with a pyrometer, allowing measurement of internal temperature, and it was also fitted with a septum which permitted the removal of gas samples using a syringe. The internal temperature was measured during the course of each reaction, and periodic gas analyses were conducted using gas chromatography. The results from these reactions are tabulated in Appendix V.

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APPENDIX I

PRODUCT ANALYSES: FATTY ACID SOAP OXIDATIONS

REACTIONS 1 AND 2

The cooled product solutions from Reactions 1 and 2 (Table I) were acidified with dilute aqueous mineral acid and extracted with hexane. The hexane extracts were dried over sodium sulfate or magnesium sulfate,and the hexane was driven off by evaporation under reduced pressure. The free acids were converted to their methyl esters in 5% methanolic hydrochloric acid (91), and the esters were analyzed by gas-liquid chromatography on an EGSS-X column. Methyl palmitate or methyl stearate was added as internal standard in each case. Only fatty acid methyl esters, but no fatty acid oxidation products, were detected in the hexane extracts.

The hexane extracted aqueous phase from Reaction 2 was further extracted with ethyl acetate, yielding an oily mixture of reaction products which weighed 966 mg. The infrared spectrum of this material was recorded. A very broad, intense absorption between 2300 and 3600 cm^{-1}, indicative of carboxylic acids, was observed. Another infrared spectrum was recorded after the acids had been converted to their methyl esters. That spectrum showed an intense, relatively broad, band in the carbonyl stretch region, 1700-1800 cm^{-1}, and an intense, broad band centered at about 3500 cm^{-1}. The latter absorption was strong evidence for the presence of hydroxy compounds, while the broadness of the carbonyl band suggested the presence of several different types of carbonyl compounds.

The material recovered in the ethyl acetate extract was analyzed by thin-layer chromatography with a number of solvent systems. This analysis showed that the product mixture consisted of a large number of compounds possessing widely varying polarities. A portion (92 mg) of the ethyl acetate extract was

next chromatographed on a 50 mL buret packed with silica gel (21 g). The column was developed with chloroform and mixtures of chloroform and methanol containing increasing amounts of methanol. Acetic acid (1%) was added to the eluting solvents. The compositions of the fractions were monitored by thin-layer chromatography, and the fractions collected were analyzed by infrared spectrophotometry both as free acids and their methyl esters. All of the fractions contained carboxylic acids, but the methyl esters of the acids collected in the first fractions showed no infrared absorption attributable to free hydroxyl groups. However, the spectra of those compounds frequently displayed several distinct bands in the carbonyl stretch region, 1700-1780 cm^{-1}. The methyl esters of the more polar compounds eluted in subsequent fractions showed increasingly strong and broad infrared absorption above 3000 cm^{-1}, indicating the presence of free hydroxyl groups.

Another chromatographic separation was then performed on the same column using another portion of the ethyl acetate extract from Reaction 2. The fractions recovered were weighed, and then converted to their methyl esters in methanolic hydrochloric acid. Of the 190 mg of material loaded onto the column, 170 mg were accounted for gravimetrically after the fractionation. The methyl esters were dissolved in pyridine and treated with hexamethyldisilazane and trimethylchlorosilane to convert them to their trimethylsilyl ethers (91). Water was added to decompose the excess silylation reagents. The silylated esters were dissolved in hexane, and the pyridine was driven off under a stream of nitrogen. Both the methyl esters and methyl ester-trimethylsilyl ethers were analyzed by gas-liquid chromatography on an EGSS-X column. The major peaks detected in each fraction, both before and after silylation, were then examined by combined gas chromatography-mass spectrometry.

The products from Reaction 2 which were identified by mass spectrometry were listed in Table XXI and their structures were shown in Fig. 15. ω-Aceto acids (XXVII) and γ-keto acids (XXVIII) were recovered in the first major fraction eluted from the silica gel column, and dicarboxylic acids (XV), beginning with nonanedioic acid, were eluted in succeeding fractions. All of these compounds were identified as their methyl esters. (The gas chromatographic retention times of the peaks associated with the aceto acids, keto acids and dicarboxylic acids did not change after treatment with the silylation reagents.) α-Hydroxy acids (XXV) were eluted following the dicarboxylic acids, and the two α-hydroxydicarboxylic acids (XXVI) were retained in the last major fraction collected. These compounds were identified by mass spectrometry as their methyl esters, and as their methyl ester-trimethylsilyl ethers.

Phthalic acid was also found and identified by mass spectrometry after fractionation of the products from Reaction 2. However, this compound was never detected in later reactions and was presumed to represent an impurity present in the linoleic acid starting material.

REACTIONS 11 AND 12

The cooled products of Reactions 11 and 12 were transferred to 250 mL volumetric flasks, which were filled to volume with deionized water. Aliquots (50 mL) of the solutions were withdrawn, acidified with mineral acid, and extracted with hexane (3 x 25 mL). Eicosanoic acid internal standard was added to the hexane extracts, and the fatty acids were converted to their methyl esters by treatment with diazomethane. The methyl esters were analyzed by gas-liquid chromatography on EGSS-X columns.

Additional aliquots (2 or 3 mL) of the original product mixtures from Reactions 11 and 12 were withdrawn and transferred to 6 mL Hypo-Vials (Pierce Chemical Co.). Known quantities of decanedioic acid were added to some of those samples. The alkaline solutions were neutralized with carbon dioxide or a slight excess of hydrochloric acid, and a few drops of ammonium hydroxide were then added to neutralize the excess acid. The samples were next freeze dried in the Hypo-Vials. The vials were capped with Teflon-rubber septa (Pierce Chemical Co.), and the salts were converted to their trimethylsilyl derivatives by a procedure similar to that described by VerHaar and DeWilt (102). Dimethylsulfoxide (0.3-1.0 mL) and a quantity of Tri-Sil concentrate (Pierce Chemical Co.) sufficient to derivatize the oxidation products (0.5-1.5 mL) were injected into the vials with a syringe, and the sealed vials were shaken for a minimum of 12 hr. Samples withdrawn from the Tri-Sil phase with a microsyringe were analyzed by gas-liquid chromatography on OV-17 and SP-2100 columns. The products from Reaction 12 were also analyzed by combined gas chromatography-mass spectrometry. The compounds identified were listed in Table XXI.

APPENDIX II

REACTION SYSTEM FOR OXIDATION OF FATTY ACID ESTERS

The reaction vessel used during oxidations of the fatty acid methyl esters was a modified 1-liter Parr bomb (Parr Instruments Co.) constructed of T316 stainless steel. The bomb was equipped with a Teflon gas inlet tube for the introduction of oxygen or steam into the bottom of the vessel, a Teflon sheathed iron-constantan thermocouple (Conex Corp.), and a gas exit port which led to a vapor relief valve, a rupture disc (Frangible Discs, Inc.) and an Ashcroft Duragauge for measurement of internal pressure. The reaction vessel is illustrated schematically in Fig. 27.

As originally conceived, the reactants were to have been preheated with steam, but this step was abandoned because the quantity of condensed water introduced into the system could not be accurately estimated or controlled.

The thermocouple, which was initially connected directly to a pyrometer, ceased operating just before Reactions 1F-21F were undertaken, and no measurements of internal temperature were attempted during any of those reactions.

The upper section of the reaction vessel was bolted to a rack and pinion gear assembly such that the sealed vessel could be lowered directly into a preheated oil bath. The oil bath consisted of a 5 gallon can insulated with polyurethane foam and filled with Ucon HTF-100 high temperature fluid. The oil bath was agitated with an electric stirrer, and its temperature was controlled with a 500 watt knife heater connected through a Precision Scientific Relay to a thermometer-thermoregulator (SGA Scientific, Inc.).

During operation, the preheated (80°C) lower half of the reaction vessel was charged with the reactants and firmly bolted to the upper assembly. The

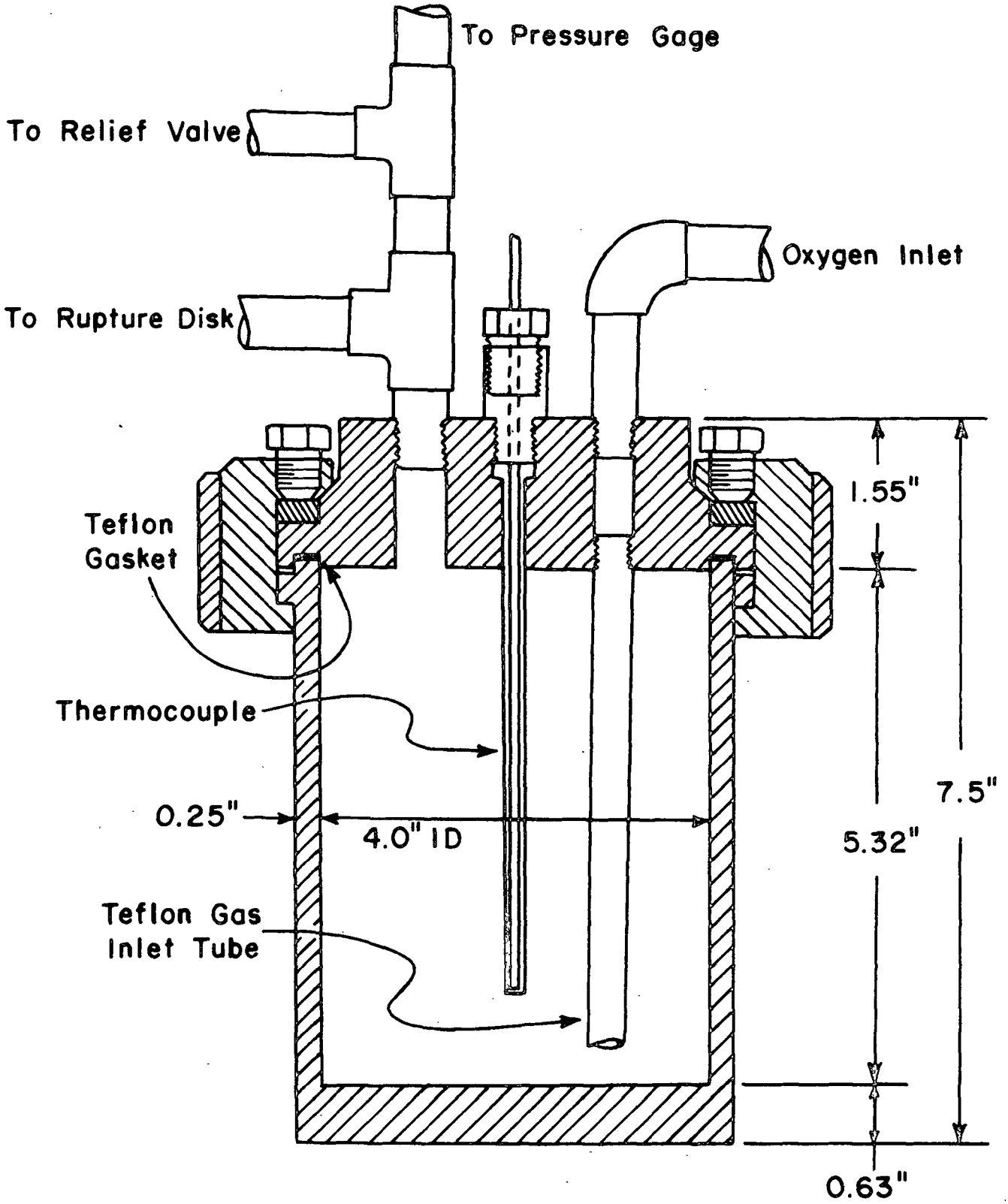


Figure 27. Details of Reaction Vessel

reactor was purged with oxygen and then pressurized through the gas inlet tube. Following the pressurization step, the charged reactor was lowered into the pre-heated oil bath. Upon completion of the reaction, the reactor was raised from the oil bath and cooled in ice water. The gases were vented to the atmosphere through the vapor relief valve, and the bomb was disassembled to allow access to its contents.

Attempts were made to collect condensible vapors by venting the reactor through a 10-ft coil of 1/8-inch stainless steel tubing immersed in ice water. However, only small amounts of condensate, consisting mostly of water, were collected, and they were not further examined.

APPENDIX III

PRODUCT ANALYSES: FATTY ACID ESTER OXIDATIONS

REACTIONS 5 AND 6

The products of Reactions 5 and 6 (Tables II and III) were filtered directly through a coarse sintered glass funnel, and the oxidized wood meal substrates were washed thoroughly with deionized water. The black liquor (water washings) from both reactions were transferred to 2000 mL volumetric flasks, which were filled to volume with water. The washed wood meal from each reaction was leached overnight in acidified acetone as described by Pearl and Dickey (3) and then extracted with acetone for 8 hr in a Soxhlet extractor. The acetone extracts were combined, concentrated on a rotary evaporator, diluted with water and extracted with ethyl acetate (3 x 150 mL). The ethyl acetate extracts were dried over sodium sulfate and transferred to 500 mL volumetric flasks, which were filled to volume with ethyl acetate.

Aliquots (50 mL) of the black liquor obtained from both reactions were then withdrawn and partitioned into polar and nonpolar phases according to the procedure of Saltsman and Kuiken (103). Fatty acids and fatty acid esters were extracted in hexane, which comprised the nonpolar phase, while many fatty acid oxidation products were retained in the polar phase, which consisted of water, acetone and methanol. Similarly, aliquots (100 mL) of the ethyl acetate-soluble acetone extracts from both reactions were fractionated according to the Saltsman-Kuiken procedure after the ethyl acetate was driven off by evaporation. Stearic acid internal standard was added to each of the four nonpolar phases obtained, and each of them was treated with diazomethane. The fatty acid methyl esters were then analyzed by gas-liquid chromatography on EGSS-X columns. Most of the fatty acids detected in the product of Reaction 5 were found in the extract

recovered from the black liquor; the fatty acid esters originally present in the system were apparently saponified during the course of the reaction with oxygen and sodium hydroxide. The soaps were then washed from the wood meal with water. Conversely, the fatty acids recovered from the product of Reaction 6 were found primarily in the acetone extract of the wood meal. The unoxidized fatty acid methyl esters did not appear to undergo extensive saponification during the reaction with carbonate, and those esters were not washed from the wood meal with water.

A larger portion (1000 mL) of the black liquor from Reaction 5 was then withdrawn and partitioned into polar and nonpolar phases. The Saltsman-Kuiken procedure was modified slightly by eliminating methanol and employing equal volumes of acetone and water only as the polar phase. Compounds recovered in the polar phase were then passed successively through beds of Amberlite IR-120 cation exchange resin (3.2 x 35 cm) and Amberlite IRA-400 anion exchange resin (3.6 x 35 cm). The anion exchange resin had been converted to its strong base form (-OH) with 1N sodium hydroxide. Organic acids retained on the anion exchanger were eluted with 5% formic acid in methanol (2500 mL). The material recovered was concentrated on a rotary evaporator, yielding a viscous, reddish-brown oil weighing 2.84 g. This was transferred to a column packed with silica gel (200 g), which was developed with chloroform and chloroform-methanol mixtures containing increasing amounts of methanol. Acetic acid (0.5%) was added to the solvents. The fractions collected were treated with diazomethane and analyzed by gas-liquid chromatography. Methyl esters of the acids recovered in the more polar fractions were also converted to their trimethylsilyl ethers. The methyl esters and methyl ester-trimethylsilyl ethers were then analyzed by combined gas chromatography-mass spectrometry.

The fractions initially collected after column chromatography of the reaction products contained ω-aceto acids (XXVII), γ-keto acids (XXVIII) and dicarboxylic acids (XV). Methyl linoleate, methyl benzoate, and a compound which appeared to be highly unsaturated were also recovered in the least polar fractions. The latter compound was presumably a lignin-derived wood oxidation product. Compounds eluted from the column in later fractions included α-hydroxy acids (XXV) and several carbohydrate-derived oxidation products.

A fraction containing ω-aceto acids and dicarboxylic acids was reduced with sodium borohydride. The reduction products were converted to their methyl ester-trimethylsilyl ethers. 9-Hydroxydecanoic acid, the reduction product of 9-oxodecanoic acid (XXVII, n=7) was tentatively identified from its mass spectrum, which is tabulated in Appendix VIII. Gas chromatographic peaks expected for reduction products of the lower ω-aceto acids were apparently obscured by peaks corresponding to the dicarboxylic acid dimethyl esters.

The nonpolar phase obtained after fractionation of the black liquor from Reaction 5 was dried over magnesium sulfate, and the hexane was driven off by evaporation under reduced pressure. Of the oil which remained (0.95 g), 0.56 g were transferred to a 50 mL buret packed with silica gel (26 g). The column was developed with hexane and mixtures of hexane and ether. Again, acetic acid (1%) was added to the solvents. Compositions of the fractions collected were monitored by thin-layer and gas-liquid chromatography. While the former technique indicated the presence of small quantities of other, more polar compounds, only linoleic acid, as its methyl ester, could be detected by gas chromatography.

An additional portion (1000 mL) of the black liquor from Reaction 6 was also partitioned into polar and nonpolar phases. The polar phase was passed successively through the cation and anion exchangers, and organic acids retained

on the latter were eluted first with carbon dioxide saturated methanol (1000 mL), and then with 5% formic acid in methanol (2000 mL). Both solutions were concentrated on a rotary evaporator, and the free acids recovered were converted to their methyl esters with diazomethane. The methyl esters were analyzed by combined gas chromatography-mass spectrometry. Although numerous gas chromatographic peaks could be detected, only three compounds, dicarboxylic acids possessing seven, eight and nine carbon atoms, were conclusively identified.

REACTION 3

The oxidized wood meal from Reaction 3 (Tables II and III), originally impregnated with methyl palmitate, was washed with 300 mL water, and then with 1200 mL acetone-methanol (2:1, v/v) containing 40 mL concentrated hydrochloric acid. The combined washing thus represented the polar phase of a Saltsman-Kuiken fractionation (103). This solution was extracted with hexane, effectively partitioning the entire product into polar and nonpolar phases. The wood meal was further extracted with acidified acetone (3), and the acetone extract was also partitioned into polar and nonpolar phases. The two polar phases recovered, and the two nonpolar phases, were combined. The combined nonpolar solution obtained was dried over magnesium sulfate, concentrated on a rotary evaporator, and brought to a volume of 100 mL in a volumetric flask. A 5-mL aliquot was withdrawn, and stearic acid internal standard was added. The sample was treated with diazomethane and analyzed by gas-liquid chromatography on an EGSS-X column. The combined polar phase from this reaction was passed successively through the regenerated ion exchange resins (Amberlite IR-120 and IRA-400). The anion exchange resin was then eluted with 5% formic acid in methanol (1500 mL). The solution recovered was dried over magnesium sulfate and concentrated to a volume of 50 mL. Portions of this solution were analyzed by gas-liquid chromatography

on an EGSS-X column after treatment with diazomethane. However, no suspected oxidation products of methyl palmitate were detected in sufficient quantity to warrant further analysis by mass spectrometry.

REACTION 4

The product of Reaction 4 (Tables II and III) was freeze dried and extracted with acetone containing a 50% excess of hydrochloric acid. The acetone extract was brought to 500 mL in a volumetric flask. Two 10 mL aliquots were withdrawn, eicosanoic acid internal standard was added to each, and each sample was analyzed by gas-liquid chromatography on EGSS-X after treatment with diazomethane. All but 50 mL of the remaining acetone extract was chromatographed on a 2.5 cm diameter column packed with silica gel (195 g). The column was developed with chloroform and mixtures of chloroform and methanol containing increasing amounts of methanol. Acetic acid (0.5%) was added to the solvents. Compositions of the fractions collected were monitored by thin-layer and gas-liquid chromatography. Selected fractions were further analyzed by gas chromatography-mass spectrometry after treatment with diazomethane. Only nonanedioic acid, octanedioic acid, and heptanedioic acid were conclusively identified.

REACTIONS 1F-21F

The products of Reactions 1F-21F (Tables V, VII, XII-XVI) were all freeze-dried. The freeze-dried products were extracted with ether for 8 hr in a Soxhlet extractor. The ether-extracted substrates (wood meal or cotton linters) were then slurried with 250 mL water containing 15 mL concentrated sulfuric acid. After standing for at least an hour, the slurry was filtered through a coarse sintered glass funnel. The substrates were washed with water (600-700 mL) and ether (100 mL). After excess water had been pressed from the substrate with a

rubber sheet and suction, both the substrate and aqueous washings were extracted with ether in continuous extractors for 24 hr. The ether extracts, including the first ether extracts of the dried oxidation products, were combined and dried over magnesium sulfate. The combined ether extracts were brought to 250 mL in volumetric flasks, and 10 mL aliquots were withdrawn for analysis.

The 10-mL aliquots of the ether extracts from all reactions were mixed with 1 mL methanol and 0.1 mL water, and the ether-methanol-water solutions were analyzed according to the scheme outlined in Fig. 28. The samples were passed through 1-cm diameter columns loaded with 12.5 g DEAE Sephadex weakly basic anion-exchange resin (Pharmacia Fine Chemicals). The DEAE Sephadex had been converted to its hydroxide form and conditioned according to the procedure of Zinkel and Rowe (62). The anion-exchange resin was then eluted successively with 350 mL 90:10:1 ether-methanol-water (v/v/v) and 1000 mL 90:10 ether-methanol saturated with carbon dioxide. Neutrals, including fatty acid methyl esters, were swept through the column with the first solvent mixture, while weak acids, including free fatty acids, were eluted with the carbon dioxide saturated solvent (62). Eicosanoic acid internal standard was added to both fractions, and both of them were treated with diazomethane. The ether was distilled off, and the samples were further concentrated to near dryness on a rotary evaporator. The methyl esters were then dissolved in ether, dried over sodium sulfate, and analyzed by gas-liquid chromatography on EGSS-X columns. Unsaponified methyl esters were thus fractionated from free fatty acids, and both were analyzed separately.

More strongly acidic fatty acid oxidation products, which were retained on the DEAE Sephadex after elution with carbon dioxide saturated ether-methanol, were stripped from the resin with alternate washings of 1N hydrochloric acid (3 x 150 mL) and 1N potassium hydroxide (3 x 150 mL) on a sintered glass funnel. The final base washing effectively regenerated the ion-exchange resin, which was

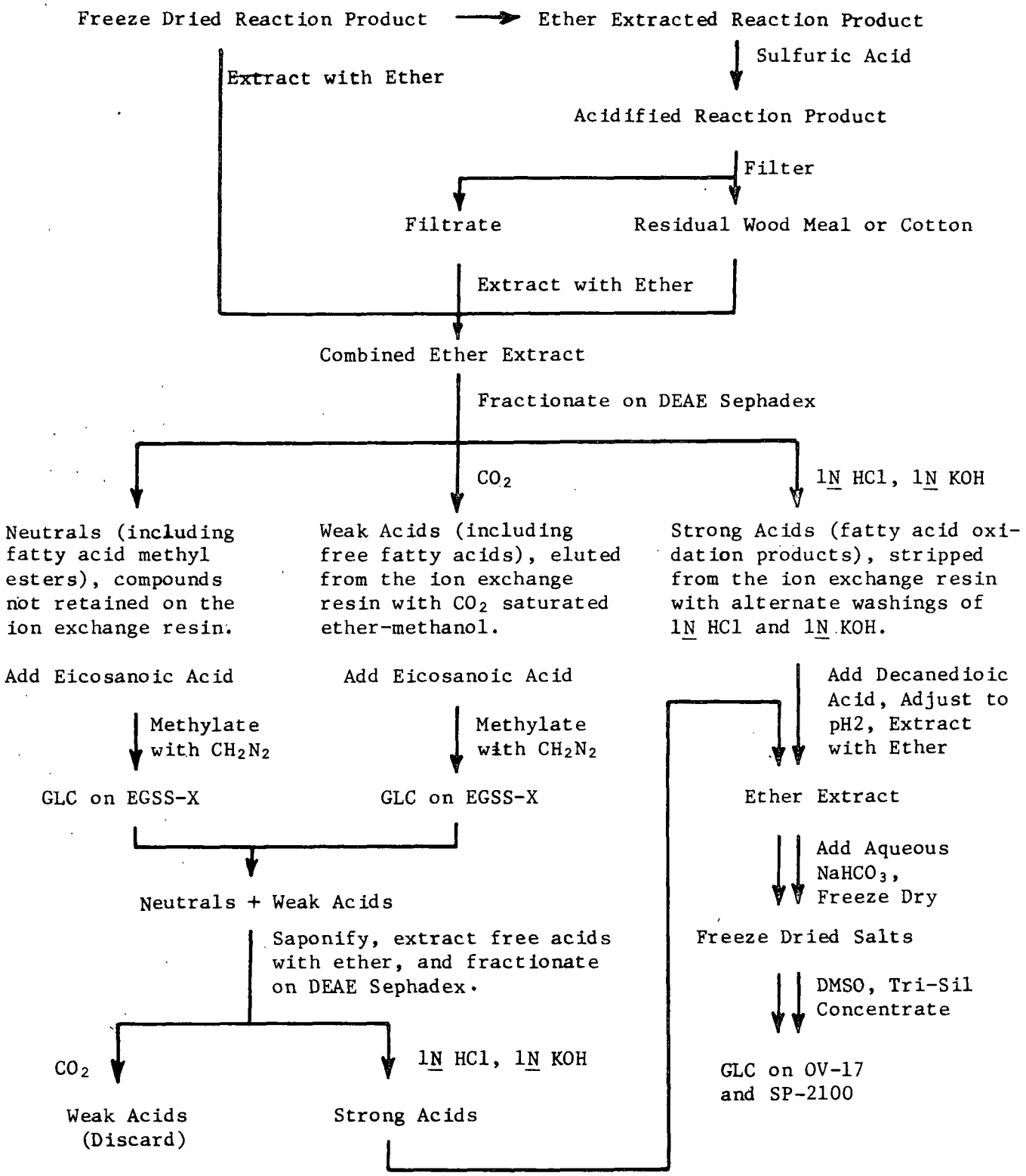


Figure 28. Analytical Procedure for Recovery and Analysis of Fatty Acid Methyl Esters, Free Fatty Acids and Fatty Acid Oxidation Products from Reactions 1F-21F

then washed with distilled water until the filtrate was neutral to pH test paper. Those washings were discarded. The filtrates from the acid and base washings, which contained the fatty acid oxidation products, were combined and adjusted to pH 2 with sulfuric acid. Decanedioic acid internal standard was added, and the aqueous solutions (900 mL) were then extracted with ether for at least 18 hr in continuous extractors. Water (2-3 mL) was then added to the ether extracts, and a small amount of sodium bicarbonate, just enough to neutralize the acids, was also added. The ether was distilled off and the aqueous salt solutions recovered were transferred to 6 mL Hypo-Vials (Pierce Chemical Co.) and freeze-dried; the vials were covered with aluminum foil and then carefully rotated in dry ice-acetone to coat the sides of the vials with the frozen material. The aluminum foil was then perforated, and the vials were placed upright in an insulated desiccator. The desiccator was immediately connected to the freeze dryer. The Hypo-Vials containing the freeze-dried oxidation products, as their sodium salts, were capped with Teflon-rubber septa (Pierce Chemical Co.), and the salts were converted to their trimethylsilyl derivatives by the method of VerHaar and DeWilt (102). Dimethylsulfoxide (0.5-1.0 mL) and enough Tri-Sil concentrate (Pierce Chemical Co.), usually 0.5-1.5 mL, to derivatize the salts, were injected into the sealed Hypo-Vials with a syringe. The vials were shaken for at least 12 hr, and samples were then withdrawn from the Tri-Sil phase with a microsyringe and injected directly into the gas chromatograph. All samples were analyzed gas chromatographically on both OV-17 and SP-2100 columns. In some instances (see Table XXI) the oxidation products were also analyzed by combined gas chromatography-mass spectrometry.

Samples from all reactions were analyzed at least twice, and in most cases three times. During the last series of analyses, the neutrals and weak acids fractions were recombined after gas chromatography and saponified in 0.5N ethanolic

potassium hydroxide. The saponified material was extracted with ether and again fractionated on DEAE Sephadex (5 g). The weak acids were eluted with 400 mL of carbon dioxide-saturated ether-methanol, and the strong acids retained on the resin were recovered by alternate washings with 1N hydrochloric acid (3 x 50 mL) and 1N potassium hydroxide (3 x 50 mL). The washings were combined, adjusted to pH 2, extracted with ether, and the acids recovered were converted to their trimethylsilyl derivatives after their sodium salts were freeze-dried. Lesser quantities of dimethylsulfoxide (0.3-0.5 mL) and Tri-Sil concentrate (0.2-1.0 mL) were generally required. The trimethylsilyl derivatives were once again analyzed by gas-liquid chromatography on OV-17 and SP-2100 columns.

REACTIONS 7 AND 8

The products of Reactions 7 and 8 (Tables II and III) were analyzed according to the same procedure just described for Reactions 1F-21F, except that the products were not first freeze-dried.

REACTIONS 22F-24F

The products of Reactions 22F-24F (Tables XI-XVI) were also analyzed according to the procedures described for Reactions 1F-21F. However, the products were not freeze-dried, and no neutrals fractions were collected, since the compounds undergoing oxidation were already free fatty acids.

REACTIONS 9 AND 10

The products of Reactions 9 and 10 (Tables II and III) were extracted with ether as described for Reactions 1F-21F, although the products were not first freeze-dried. The ether extracts were brought to 250 mL in volumetric flasks, and 200 mL aliquots were withdrawn. These were fractionated on DEAE Sephadex (75 g) in a 2.5-cm diameter column. Weak acids were eluted with 4000 mL 90:10 ether-methanol

saturated with carbon dioxide, and the strong acids were stripped from the resin with alternate washings of 1N hydrochloric acid (3 x 300 mL) and 1N potassium hydroxide (3 x 300 mL). The acid and base washings were combined, adjusted to pH 2, and extracted with ether for 24 hr in continuous extractors. Water (5 mL) and enough sodium bicarbonate to neutralize the acids were added to the extracts, and the ether was distilled off. The aqueous solutions recovered were freeze-dried, transferred to 3 mL Reacti-Vials (Pierce Chemical Co.), and treated with dimethylsulfoxide (1 mL) and Tri-Sil concentrate (1.5 mL). The fatty acid oxidation products were then analyzed as their trimethylsilyl derivatives by combined gas chromatography-mass spectrometry on OV-17, SP-2100 and QF-1 columns. The compounds identified were listed in Table XXI.

APPENDIX IV

REACTIONS OF FATTY ACID OXIDATION PRODUCTS WITH OXYGEN-ALKALI

Selected fatty acid oxidation products were allowed to react with oxygen in the presence of cotton and both sodium hydroxide and sodium bicarbonate. The cotton was washed thoroughly with water, and the washings were acidified and extracted with ether for at least 18 hr in continuous extractors. Portions of the ether extracts were withdrawn for analysis. Water (2-3 mL) and a slight excess of sodium bicarbonate were added. The ether was distilled off, and the salts recovered were freeze dried and converted to their trimethylsilyl derivatives as described in Appendix III. Shown in Table XXII are the relative peak areas of the reactants and their oxidation products for each of the six reactions carried out.

TABLE XXII

OXIDATIONS OF SELECTED COMPOUNDS[a]

	Reactant (Acid)		Oxidation Product (Acid)	
Alkali	Compound	Relative Peak Area[b]	Compound	Relative Peak Area[b]
11 g NaOH	0.88 g Nonanedioic	1.00	None detected	
23.1 g $NaHCO_3$	0.52 g Nonanedioic	1.00	None detected	
11 g NaOH	0.18 g 2-Hydroxydecanedioic	1.00	None detected	
	0.13 g 2-Hydroxydecanoic	1.00	None detected	
23.1 g $NaHCO_3$	0.16 g 2-Hydroxydecanedioic	0.71	Nonanedioic	0.29
	0.10 g 2-Hydroxydecanoic	0.75	Nonanoic	0.25
11 g NaOH	0.57 g 9,10-Dihydroxystearic	1.00	None detected	
23.1 g $NaHCO_3$	0.58 g 9,10-Dihydroxystearic	0.98	Nonanedioic	0.01
			Nonanoic	0.01

[a] All reactions were carried out in the presence of cotton at 130° C for 5 hr under an initial oxygen pressure of 2100 kPa.

[b] Defined such that the sum of the relative peak areas from a reactant and its oxidation products adds up to unity.

APPENDIX V

OXIDATIONS OF FATTY ACID METHYL ESTERS WITH SUBSTRATE: TEMPERATURE RISE AND GAS ANALYSES

Three supplementary reactions were carried out utilizing wood meal or cotton linters impregnated with about 2 g each of methyl linoleate and methyl oleate. The reaction products were not analyzed, but the temperature profiles within the reactor were measured, and gas analyses were conducted using gas chromatography. The reaction conditions are summarized in Table XXIII, the temperature profiles are shown in Table XXIV, and the results of the gas analyses are presented in Table XXV.

TABLE XXIII

SUPPLEMENTARY REACTIONS: REACTION CONDITIONS

Reaction No.	Temperature, °C	O_2 Pressure, kPa	Alkali	Substrate
1A	160	690	11 g NaOH	Wood meal
2A	160	690	23.1 g $NaHCO_3$	Cotton linters
3A	100	690	11 g NaOH	Wood meal

Gas samples were collected in a Teflon bag or withdrawn directly from the reaction vessel with a Pressure Lok syringe (Supelco, Inc.). The gas samples to be analyzed (4 mL) were injected into the gas chromatograph with the same syringe. The gases were analyzed on a 6 ft, 1/8-inch diameter column packed with 120/140 Carbosieve. The column temperature was initially 45°C, and this was increased to 175°C at a rate of 30°/min after the oxygen peak was recorded (about 3 min). Carbon dioxide was eluted about 5 min later. The injector and detector temperatures were 200°C, and the carrier gas was prepurified helium (Matheson Gas Products). The carrier gas flow rate was 30 mL/min.

TABLE XXIV

SUPPLEMENTARY REACTIONS: TEMPERATURE AND PRESSURE PROFILES

Time, min	Reaction 1A		Reaction 2A		Reaction 3A	
	Temperature, °C	Pressure, kPa	Temperature, °C	Pressure, kPa	Temperature, °C	Pressure, kPa
0	75	689	65	689	75	689
5	85	800	77	820	83	716
10	110	868	105	896	90	730
15	125	896	115	958	95	737
20			120	1020	97	737
25					98	737
30	145	950	130	1090	100	737
45					100	733
60	160	937	145	1270	100	710
90					100	689
120			160	1380	100	662
180	160	826			100	620
300	160	840	160	1240	100	579

TABLE XXV

SUPPLEMENTARY REACTIONS: GAS ANALYSES

Reaction No.	Time, hr	Relative Peak Areas[a]		
		Oxygen	Carbon Dioxide	Carbon Monoxide
Calibration Mixture[b]		0.875	0.125	
1A	5	0.69	0.29	0.02
2A	2	0.58	0.41	0.01
	5	0.32	0.67	0.01
3A	5	1.00	0	0

[a]Defined such that the sum of the areas is unity.

[b]The calibration mixture consisted of 90% oxygen and 10% carbon dioxide.

APPENDIX VI

GAS-LIQUID CHROMATOGRAPHY

Gas chromatographic columns and the conditions employed during their operation are described in Table XXVI. Generally, fatty acid methyl esters and the methyl esters or methyl ester-trimethylsilyl ethers of fatty acid oxidation products were analyzed on polyester-silicone columns (EGSS-X), while fatty acid oxidation products were analyzed as their trimethylsilyl derivatives on the various silicone columns (SP-2100, OV-17 or QF-1). Oxidation products were analyzed on both OV-17 and SP-2100 columns since neither could effectively separate all the compounds of interest, but each provided good separation of major peaks not resolved by the other. The QF-1 column was used mainly during mass spectral studies as a supplement to the other columns. The operating conditions outlined in Table XXVI were representative of those which were normally used. However, the conditions were sometimes changed, particularly when an analysis was performed in conjunction with mass spectrometry, in attempts to obtain improved resolution of specific compounds.

Shown in Fig. 29 is a representative chromatogram of three fatty acid methyl esters separated on an EGSS-X column. The three compounds are methyl oleate, methyl linoleate, and methyl eicosanoate. The last compound was used as an internal standard during analysis of the other two. The column provides good separation of fatty acid methyl esters both according to molecular weight and degree of unsaturation. Methyl palmitate and methyl stearate, also used as internal standards, have shorter retention times than methyl oleate and are well separated from each other. However, because of high column bleed, the EGSS-X columns deteriorated with time, and retention times of all compounds decreased during use. Because they gradually lost effectiveness, several different columns were used during the course of this investigation.

TABLE XXVI

GAS CHROMATOGRAPHIC COLUMNS AND OPERATING CONDITIONS

Column[a] Length, ft	Liquid Phase	Support	Column Temperature			Detector Temp., °C	Injector Temp., °C	Carrier Gas and Flow Rate
			Initial	Rate	Final, °C			
6	10% EGSS-X	100/120 Gas Chrom P	170-190°C	Isothermal		250	235	30 mL/min N_2, 25 mL/min He
6	10% SP-2100	80/100 Supelcoport	120°C, 8 min	2°/min	250	270	250	20 mL/min He
6	3% SP-2100	100/120 Supelcoport	100°C, 8 min	2°/min	250	270	250	20 mL/min He
9	3% OV-17	80/100 Supelcoport	100°C, 8 min	2°/min	250	270	250	20 mL/min He
10	3% QF-1	100/120 Gas Chrom Q	80°C, 5 min	2°/min	250	270	250	20 mL/min He

[a]All columns were 1/8-inch stainless steel tubing.

The fatty acid methyl esters all had very similar detector responses. When methyl palmitate or methyl stearate was used as internal standard, the weight response factors of methyl oleate and methyl linoleate, defined according to Equation (51), were unity.

$$F_x = (W_x)(A_I)/(W_I)(A_x), \tag{51}$$

where F_x = weight response factor of compound x

W_x = weight of compound x

W_I = weight of internal standard

A_x = peak area corresponding to compound x

A_I = peak area corresponding to internal standard

The weight response factors calculated for methyl oleate and methyl linoleate were both 0.99 with respect to the methyl eicosanoate internal standard. The response factors of all compounds, including the fatty acid oxidation products, were determined by preparing control mixtures of authentic compounds and measuring their peak areas from gas chromatograms recorded under conditions within the limits of those used during the actual product analyses. In most cases, response factors were determined with data obtained from two or more separate control mixtures and from at least three different chromatograms of each mixture.

Listed in Table XXVII are the retention times and weight response factors, determined with respect to the decanedioic acid internal standard used throughout the study, of the major fatty acid oxidation products, analyzed as their trimethylsilyl derivatives. Representative chromatograms of the silylated products, separated on the OV-17 column, were reproduced in Fig. 16 and 17.

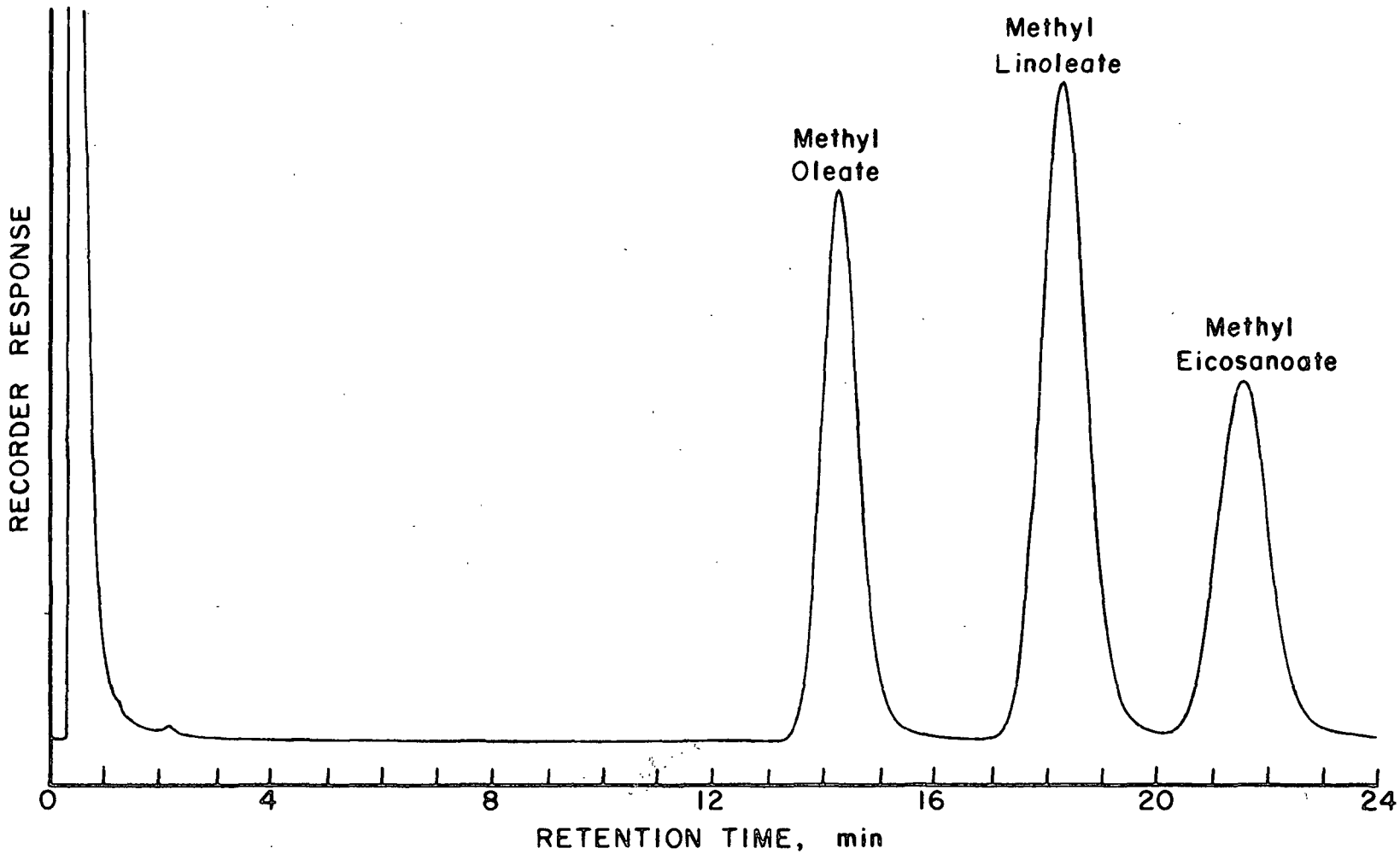


Figure 29. Gas Chromatogram of Fatty Acid Methyl Esters. Column: EGSS-X, Column Temperature: 170°C, Carrier Gas and Flow Rate: 25 mL/min He

TABLE XXVII

RETENTION TIMES AND WEIGHT RESPONSE FACTORS

Compound	OV-17 Column[a] Retention Time, min	OV-17 Column[a] Response Factor[c]	SP-2100 Column[b] Retention Time, min	SP-2100 Column[b] Response Factor[c]
Heptanoic acid	6.8	0.9[d]	9.2	0.9[d]
Octanoic acid	11.5	0.9[d]	14.5	0.9[d]
Nonanoic acid	17.1	0.9	20.4	0.9
Succinic acid	16.9	0.9[d]	17.6	0.9[d]
Pentanedioic acid	22.1	0.9[d]	23.1	0.9[d]
Hexanedioic acid	28.6	0.9	29.3	0.9
Heptanedioic acid	34.5	0.9	35.2	0.9
Octanedioic acid	40.0	0.9	40.5	0.9
Nonanedioic acid	45.3	0.9	46.0	0.9
Decanedioic acid	50.5	I.S.	51.2	I.S.
2-Hydroxybutyric acid	4.4	0.7	7.7	0.7
2-Hydroxypentanoic acid	7.5	0.7	11.4	0.7
2-Hydroxyhexanoic acid	11.7	0.7[d]	16.2	0.7[d]
2-Hydroxyheptanoic acid	16.8	0.7[d]	21.6	0.7[d]
2-Hydroxyoctanoic acid	22.0	0.7[d]	27.0	0.7[d]
2-Hydroxynonanoic acid	27.4	0.7[d]	32.5	0.7[d]
2-Hydroxydecanoic acid	32.7	0.7	38.1	0.7
Malic acid	25.8	0.9	29.3	0.9
2-Hydroxypentanedioic acid	31.5	0.9[d]	34.7	0.9[d]
2-Hydroxyhexanedioic acid	37.3	0.9[d]	40.2	0.9[d]
2-Hydroxyheptanedioic acid	42.8	0.9[d]	45.5	0.9[d]
2-Hydroxyoctanedioic acid	47.6	0.9[d]	50.3	0.9[d]
2-Hydroxynonanedioic acid	52.6	0.9[d]	55.2	0.9[d]
2-Hydroxydecanedioic acid	57.4	0.9	59.6	0.9
6-Hydroxyhexanoic acid	21.6	0.7[d]	24.8	0.7[d]
7-Hydroxyheptanoic acid	27.2	0.7[d]	30.6	0.7[d]
8-Hydroxyoctanoic acid	32.9	0.7[d]	36.5	0.7[d]
9,10-Dihydroxystearic acid				
Low Melting Isomer	76.8	0.9	80.9	0.8
High Melting Isomer	77.1	0.9[d]	81.5	0.8[d]
Trihydroxy Octadecenoic acids	79.5-81.0		85.0-86.0	

[a] Column: 9 ft, 3% OV-17 on 80/100 Supelcoport. Column temperature: 100°C for 8 min, then 2°/min to 250°C. Carrier gas: 20 mL/min He.

[b] Column: 6 ft, 3% SP-2100 on 100/120 Supelcoport. Column temperature: 100°C for 8 min, then 2°/min to 250°C. Carrier gas: 20 mL/min He.

[c] Weight response factors calculated with respect to decanedioic acid according to equation (51).

[d] Estimates only; response factors were not actually determined for these compounds.

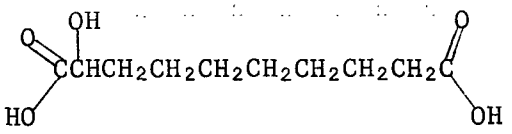
APPENDIX VII

PROTON NMR SPECTRA OF SYNTHESIZED COMPOUNDS

TABLE XXVIII

NMR SPECTRUM OF 2-HYDROXYDECANEDIOIC ACID

δ, ppm	Multiplicity	No. of Protons	Assignment
1.37	Multiplet	10	c - g
1.62	Multiplet	2	b
2.31	Triplet	2	h
4.16	Multiplet	1	a



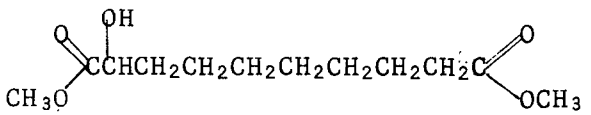
a b c d e f g h

TABLE XXIX

NMR SPECTRUM OF DIMETHYL 2-HYDROXYDECANEDIOATE

δ, ppm	Multiplicity	No. of Protons	Assignment
1.34	Multiplet	10	d - h
1.61	Multiplet	2	c
2.32	Triplet	2	i
2.83	Multiplet	1	k
3.62	Singlet	3	j
3.70	Singlet	3	a
4.12	Multiplet	1	b

k



b c d e f g h i

a j

TABLE XXX

NMR SPECTRUM OF 2-HYDROXYDECANOIC ACID

δ, ppm	Multiplicity	No. of Protons	Assignment
0.91	Triplet	3	i
1.33	Multiplet	12	c - h
1.70	Multiplet	2	b
4.16	Multiplet	1	a

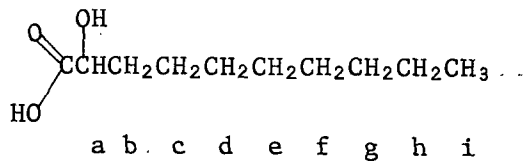


TABLE XXXI

NMR SPECTRUM OF METHYL 2-HYDROXYDECANOATE

δ, ppm	Multiplicity	No. of Protons	Assignment
0.90	Triplet	3	j
1.31	Multiplet	12	d - i
2.84	Multiplet	1	k
3.69	Singlet	3	a
4.10	Multiplet	1	b

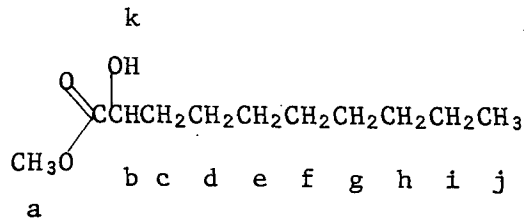


TABLE XXXII

NMR SPECTRUM OF 9-HYDROXYNONANOIC ACID

δ, ppm	Multiplicity	No. of Protons	Assignment
1.36	Multiplet	12	b - g
2.30	Triplet	2	a
3.55	Multiplet	2	h

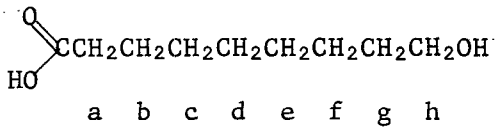
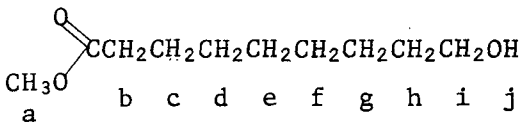


TABLE XXXIII

NMR SPECTRUM OF METHYL 9-HYDROXYNONANOATE

δ, ppm	Multiplicity	No. of Protons	Assignment
1.32	Multiplet	12	c - h
2.31	Triplet	2	b
2.84	Multiplet	1	j
3.52	Triplet	2	i
3.61	Singlet	3	a



APPENDIX VIII

COMBINED GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Analysis by combined gas chromatography-mass spectrometry was conducted with a Du Pont 21-491 mass spectrometer coupled to a Varian Aerograph 1400 gas chromatograph as described in the Experimental Section. A number of different gas chromatographic columns were utilized and the chromatographic conditions varied widely, depending on the limitations of the column and the objectives of the analysis. However, the conditions listed in Table XXVI of Appendix VI were typical of those employed.

Samples were diverted to the mass spectrometer by a splitter valve located ahead of the detector on the gas chromatograph. During analysis the separator block housing the splitter valve and the line feeding the mass spectrometer were maintained at a temperature of 300°C. Prior to sample introduction, the internal pressure of the mass spectrometer was usually $0.7\text{-}2.0 \times 10^{-7}$ torr. Other operating conditions and control settings were: source temperature, 200-225°C; oven temperature, 100-120°C; ionizing voltage, 75 ev; filament setting, G.C.; sensitivity, 4-9; scan rate, 10 or 100 sec/decade; recorder chart speed, 4 inches/sec. Determinations of mass-to-charge ratios for the observed peaks were aided by addition of perfluorotributylamine internal standard during analysis.

Mass spectra are listed in Tables XXXIV-L. Each table contains the mass spectra of all compounds belonging to a particular class as one specific derivative. Mass spectra of identified reaction products and authentic compounds are included in the same tables to facilitate their comparisons. Shown in Fig. 30-44 are interpretations of all the spectra which are tabulated. The interpretations emphasize characteristics unique or essential to the spectra involved.

TABLE XXXIV

MASS SPECTRA OF MONOCARBOXYLIC ACID TRIMETHYLSILYL ESTERS

Pentanoic acid (XIV, n=3)
Trimethylsilyl derivative of
product from reaction 23F

m/e	%	m/e	%
72	3	116	4
73	80	117	28
74	11	118	3
75	100	119	1
76	9	120	2
77	6	129	4
85	2	132	12
87	1	133	4
88	2	145	3
91	3	146	3
100	2	147	2
101	1	159	62
102	1	160	12
115	3	161	3

Nonanoic acid (XIV, n=7)
Trimethylsilyl derivative of
product from reaction 21F

m/e	%	m/e	%
72	4	132	29
73	100	133	5
74	8	143	3
75	76	145	17
76	8	146	2
77	7	147	24
78	8	148	6
81	9	149	5
83	8	157	2
89	3	159	2
93	4	171	3
103	9	172	2
105	3	173	28
116	3	174	5
117	59	175	2
118	8	215	95
119	4	216	17
129	23	217	4
131	20	230	3

Heptanoic acid (XIV, n=5)
Trimethylsilyl derivative of
product from reaction 23F

m/e	%	m/e	%
73	54	129	19
74	13	131	21
75	77	132	14
76	7	133	8
77	7	147	9
78	10	187	100
109	12	188	9
111	7	189	8
117	28		

Octanoic acid (XIV, n=6)
Trimethylsilyl derivative of
product from reaction 23F

m/e	%	m/e	%
73	87	131	32
74	8	132	22
75	81	144	6
76	17	145	14
103	14	147	15
109	5	157	8
117	38	201	100
118	12	202	11
129	14	203	6

Nonanoic acid (XIV, n=7)
Trimethylsilyl derivative of
authentic compound

m/e	%	m/e	%
72	3	130	3
73	62	131	13
74	10	132	31
75	66	145	12
76	4	146	3
77	6	159	3
81	8	171	7
98	5	215	100
116	7	216	15
117	55	217	4
129	10	230	3

TABLE XXXV

MASS SPECTRA OF DICARBOXYLIC ACID DIMETHYL ESTERS

Succinic acid (XV, n=2)
Dimethyl ester of product from reaction 12. Reference: CRC Handbook of Spectral Data (103)

m/e	%	m/e	%
41	7	73	22
43	30	81	7
45	7	83	8
50	7	87	20
52	7	101	10
54	6	114	35
55	27	115	100
56	6	116	10
59	26	117	11
64	9	119	14
69	5		

Hexanedioic acid (XV, n=4)
Dimethyl ester of product from reaction 5. Reference: Ryhage and Stenhagen (67)

m/e	%	m/e	%
39	29	83	35
40	8	84	6
41	58	85	5
42	35	86	2
43	56	87	29
44	18	88	9
45	20	97	9
53	11	98	4
54	21	99	4
55	96	100	5
56	17	101	62
57	14	102	5
58	5	110	3
59	100	111	59
67	2	112	9
68	10	113	5
69	20	114	86
71	11	115	32
72	14	116	3
73	52	130	2
74	58	131	2
75	2	142	29
81	4	143	53
82	21	144	7

Pentanedioic acid (XV, n=3)
Dimethyl ester of product from reaction 12

m/e	%	m/e	%
55	37	88	4
57	7	96	10
59	58	97	15
63	11	100	58
81	13	101	37
83	4	113	8
85	12	127	8
87	24	128	40
		129	100

Heptanedioic acid (XV, n=5)
Dimethyl ester of product from reaction 2

m/e	%	m/e	%
27	5	74	96
29	15	81	6
39	10	82	6
41	36	83	61
42	12	84	3
43	57	87	25
44	29	88	4
45	17	96	8
48	20	97	27
49	20	100	12
53	11	101	6
54	11	111	14
55	82	112	4
56	9	113	6
57	8	114	7
58	2	115	100
59	81	116	6
67	13	124	22
68	15	125	50
69	65	128	21
70	2	129	5
71	3	156	15
72	6	157	32
73	32	158	4
		159	1

TABLE XXXV (Continued)

MASS SPECTRA OF DICARBOXYLIC ACID DIMETHYL ESTERS

Heptanedioic acid (XV, n=5)

m/e	%	m/e	%
27	20	56	4
31	7	57	8
39	15	58	2
40	5	59	74
41	36	63	6
42	14	67	3
43	63	68	25
44	5	69	63
45	18	70	8
48	12	71	3
49	12	72	3
54	9	73	52
55	86	74	98

Dimethyl ester of authentic compound

m/e	%	m/e	%
75	5	111	13
79	4	113	3
81	3	114	5
83	61	115	100
84	4	116	5
85	5	124	28
87	25	125	42
88	5	126	4
96	7	128	21
97	33	129	4
98	4	156	7
100	14	157	38
101	6	158	2

Octanedioic acid (XV, n=6)
Dimethyl ester of product from reaction 2

m/e	%	m/e	%
29	8	82	9
31	3	83	37
39	7	84	9
40	7	85	7
41	40	87	33
42	5	97	84
43	41	99	4
44	11	101	14
45	7	109	3
54	4	110	26
55	44	111	19
56	15	112	3
57	8	114	10
68	9	128	6
69	73	129	95
70	9	130	10
72	7	137	2
73	6	138	84
74	100	139	15
75	8	140	3
81	4	142	10
		171	70
		172	6

Octanedioic acid (XV, n=6)
Dimethyl ester of authentic compound

m/e	%	m/e	%
27	10	85	3
29	10	87	36
39	7	88	3
41	39	96	6
42	11	97	73
43	47	98	6
44	4	99	4
45	9	101	7
53	7	110	20
55	47	111	21
56	13	112	6
57	5	113	6
59	38	114	12
67	6	128	8
68	14	129	100
69	77	130	11
70	8	138	81
73	8	139	24
74	88	142	7
75	8	143	4
81	4	170	4
82	8	171	63
83	36	172	9
84	13		

TABLE XXXV (Continued)

MASS SPECTRA OF DICARBOXYLIC ACID DIMETHYL ESTERS

Nonanedioic acid (XV, n=7) Dimethyl ester of product from reaction 2. Reference: Ryhage and Stenhagen (67)

m/e	%	m/e	%
29	27	85	7
31	7	87	35
39	18	95	5
41	41	96	5
42	14	97	32
43	61	98	23
44	14	99	6
45	11	101	11
53	9	107	6
54	6	108	3
55	100	110	4
56	9	111	90
57	7	112	9
59	43	115	4
63	10	124	30
67	18	125	28
68	10	130	5
69	44	135	7
70	5	137	5
71	5	142	4
73	9	143	46
74	98	144	4
75	9	151	4
79	4	152	93
80	8	153	10
81	7	184	8
82	22	185	53
83	76	186	9
84	32		

Nonanedioic acid (XV, n=7) Dimethyl ester of authentic compound

m/e	%	m/e	%
27	16	85	6
29	21	87	29
39	13	88	9
41	40	96	16
42	16	97	34
43	62	98	33
45	4	101	17
49	5	107	5
53	6	110	9
55	93	111	49
56	8	112	14
57	10	113	5
59	44	124	24
63	6	125	18
69	46	128	9
70	7	129	3
73	9	130	11
74	97	142	5
75	5	143	62
77	8	144	6
79	6	152	100
80	6	153	22
81	12	156	8
82	8	184	5
83	74	185	52
84	42	186	8

TABLE XXXVI

MASS SPECTRA OF DICARBOXYLIC ACID DITRIMETHYLSILYL ESTERS

Succinic acid (XV, n=2)
Trimethylsilyl derivative of
product from reaction 12

m/e	%	m/e	%
72	11	143	4
73	100	145	5
74	22	147	100
75	89	148	66
76	8	149	34
77	7	150	4
100	4	163	4
102	10	172	16
103	5	173	11
115	5	188	4
116	7	216	3
117	13	217	7
129	31	247	55
130	5	248	10
131	9	249	5
133	10		

Succinic acid (XV, n=2)
Trimethylsilyl derivative of
product from reaction 23F

m/e	%	m/e	%
73	40	145	1
74	9	147	100
75	20	148	9
116	4	149	7
117	3	172	4
129	8	218	2
130	2	219	2
133	3	247	34
141	2	248	5
143	3	249	2

Succinic acid (XV, n=2)
Trimethylsilyl derivative of
authentic compound

m/e	%	m/e	%
72	5	133	1
73	89	145	1
74	7	147	100
75	45	148	13
76	3	149	7
77	2	172	2
113	2	173	2
115	1	221	1
116	2	247	11
117	1	248	3
129	7	249	1
130	1	262	0.3
131	1		

Pentanedioic acid (XV, n=3)
Trimethylsilyl derivative of
product from reaction 23F

m/e	%	m/e	%
73	83	149	19
74	11	158	34
75	19	159	14
77	7	171	5
99	10	173	7
103	8	174	6
117	18	186	8
129	6	187	12
130	8	203	32
131	7	204	25
133	11	233	17
135	8	261	92
141	6	262	16
147	100	263	6
148	20		

TABLE XXXVI (Continued)

MASS SPECTRA OF DICARBOXYLIC ACID DITRIMETHYLSILYL ESTERS

Hexanedioic acid (XV, n=4)
Trimethylsilyl derivative of
product from reaction 10

m/e	%	m/e	%
73	100	148	5
74	5	149	8
75	32	159	25
77	16	171	7
83	15	172	14
85	9	173	3
87	4	185	6
99	4	187	8
100	6	188	6
101	6	190	6
103	6	191	4
111	45	204	6
112	6	205	5
115	6	215	5
116	7	217	21
117	20	218	4
124	4	220	6
125	5	231	5
129	6	233	4
132	4	245	4
133	10	246	3
134	6	247	5
135	4	275	30
141	11	276	21
142	9	277	7
147	42		

Hexanedioic acid (XV, n=4)
Trimethylsilyl derivative of
authentic compound

m/e	%	m/e	%
72	5	141	26
73	100	142	5
74	13	143	3
75	74	147	47
76	6	148	12
77	3	149	10
81	3	159	17
83	24	172	19
89	3	173	4
99	5	185	12
111	61	186	3
112	4	201	3
116	4	204	8
117	11	217	13
129	13	218	6
130	5	275	45
131	3	276	6
132	4	277	4
133	4	290	1

TABLE XXXVI (Continued)

MASS SPECTRA OF DICARBOXYLIC ACID DITRIMETHYLSILYL ESTERS

Heptanedioic acid (XV, n=5)
Trimethylsilyl derivative of
product from reaction 10

m/e	%	m/e	%
72	2	147	50
73	100	148	4
74	9	149	7
75	93	155	28
76	10	156	2
81	10	157	4
92	4	171	2
97	9	173	18
111	4	199	3
113	2	204	4
117	4	209	2
125	23	214	2
129	9	217	8
132	2	245	3
133	2	247	3
143	7	289	30
145	2	290	2

Octanedioic acid (XV, n=6)
from reaction 10

m/e	%	m/e	%
72	4	109	2
73	100	110	2
74	8	111	6
75	73	116	4
77	3	117	20
79	3	121	4
83	11	129	20
93	6	130	3
95	10	132	2
97	10	133	4
99	3	138	8
101	1	139	18
103	2	143	3

Heptanedioic acid (XV, n=5)
Trimethylsilyl derivative of
authentic compound.

m/e	%	m/e	%
72	8	132	3
73	100	133	6
74	13	147	40
75	89	148	8
76	10	149	15
77	1	155	49
79	11	156	7
81	14	157	6
83	11	171	7
96	4	173	29
97	14	174	3
116	8	186	13
117	24	187	4
124	2	204	6
125	43	217	17
126	6	218	4
129	25	289	49
130	3	290	13
131	5	291	6

Trimethylsilyl derivative of product

m/e	%	m/e	%
145	3	185	8
147	23	187	23
148	4	188	3
149	14	200	3
150	4	204	5
151	2	205	2
155	1	206	2
157	1	213	2
159	2	217	11
169	23	218	3
170	5	243	2
171	5	257	3
173	3	303	18
		304	4

TABLE XXXVI (Continued)

MASS SPECTRA OF DICARBOXYLIC ACID DITRIMETHYLSILYL ESTERS

Octanedioic acid (XV, n=6) compound

m/e	%	m/e	%
72	4	111	7
73	100	117	27
74	13	118	3
75	97	121	3
76	6	129	32
77	6	130	5
81	2	131	4
83	19	132	6
93	10	133	4
95	16	138	15
97	21	139	23
109	5	141	3
110	6	143	2

Nonanedioic acid (XV, n=7) Trimethylsilyl derivative of product from reaction 10

m/e	%	m/e	%
72	6	132	5
73	100	133	4
74	12	135	5
75	68	143	2
76	4	147	26
79	7	149	21
81	6	150	3
83	9	152	18
93	10	153	6
94	3	169	4
95	4	171	5
97	8	172	3
107	6	183	3
109	5	185	6
111	6	187	3
117	16	199	5
118	5	201	20
123	3	202	4
124	5	204	10
125	3	217	8
129	24	243	2
130	3	317	30
131	4	318	8

Trimethylsilyl derivative of authentic

m/e	%	m/e	%
145	3	187	47
147	29	200	4
148	7	204	14
149	22	213	4
151	3	217	18
155	3	218	7
157	6	219	2
169	33	243	4
170	6	257	6
171	9	303	60
172	3	304	22
185	10	305	4
186	4	318	1

Nonanedioic acid (XV, n=7) Trimethylsilyl derivative of authentic compound

m/e	%	m/e	%
72	5	145	4
73	100	147	32
74	6	148	2
75	85	149	24
76	11	150	4
77	6	151	2
79	5	152	22
81	9	153	8
83	13	157	2
93	5	171	4
95	3	183	3
97	15	185	4
107	12	188	3
109	7	199	8
111	10	200	3
116	10	201	30
117	24	202	8
123	5	204	21
124	5	214	4
125	4	217	5
129	29	218	2
130	7	271	7
131	4	317	73
132	2	318	22
133	4	319	9
143	3	332	1

TABLE XXXVII

MASS SPECTRA OF α-HYDROXY ACID METHYL ESTERS

2-Hydroxyhexanoic acid (XXIV, n=3) Methyl ester of product from reaction 12

m/e	%	m/e	%
41	30	85	4
43	8	87	59
44	17	88	6
55	3	90	6
57	9	103	8
59	9	115	4
69	100		

2-Hydroxyheptanoic acid (XXIV, n=4) Methyl ester of product from reaction 12

m/e	%	m/e	%
41	15	79	3
42	4	82	5
43	27	83	100
44	7	84	4
45	41	87	4
55	70	89	4
57	22	90	27
59	20	99	1
69	10	101	77
70	6	113	2
71	14	114	3
73	8	115	2
74	5	116	4
76	5	129	5

TABLE XXXVIII

MASS SPECTRA OF α-HYDROXY ACID METHYL ESTER-TRIMETHYLSILYL ETHERS

2-Hydroxyhexanoic acid (XXIV, n=3) Methyl ester-trimethylsilyl ether of product from reaction 2

m/e	%	m/e	%
41	12	74	14
42	4	75	12
43	14	89	37
44	6	90	4
45	11	91	4
47	8	101	5
55	5	102	2
56	6	103	24
57	7	104	5
58	2	105	3
59	17	159	49
61	5	160	8
69	16	161	5
70	2	162	2
71	3	203	21
72	2	204	2
73	100		

2-Hydroxyheptanoic acid (XXIV, n=4) Methyl ester-trimethylsilyl ether of product from reaction 2

m/e	%	m/e	%
41	5	91	5
43	3	101	1
45	6	103	27
55	16	104	3
57	3	105	1
59	9	119	7
60	3	129	3
61	3	159	4
72	2	161	4
73	100	173	76
74	9	174	11
75	17	175	2
83	24	217	16
89	40	218	3
90	4		

TABLE XXXIX

MASS SPECTRA OF α-HYDROXY ACID TRIMETHYLSILYL ESTER-ETHERS

Glycolic acid
Trimethylsilyl derivative of
product from reaction 9.
Reference: Petersson (69)

m/e	%	m/e	%
73	100	147	100
74	13	148	77
75	27	149	52
81	11	150	5
88	12	161	28
89	7	162	4
95	7	163	4
103	13	177	68
115	4	178	12
117	19	179	7
119	4	189	7
131	67	190	4
133	41	205	84
134	4	206	17
135	3	207	8

2-Hydroxybutyric acid (XXIV, n=1)
Trimethylsilyl derivative of
product from reaction 10

m/e	%	m/e	%
73	70	133	8
74	8	147	80
75	18	148	14
78	7	149	8
81	7	190	11
115	3	191	3
117	5	205	15
131	100	206	2
132	12	233	7

Lactic acid (XXIV, n=0)
Trimethylsilyl derivative of
product from reaction 9.
Reference: Petersson (69)

m/e	%	m/e	%
73	100	133	11
74	10	147	88
75	14	148	12
87	4	149	9
101	3	189	21
117	60	190	9
118	7	219	9
131	4	220	3

2-Hydroxybutyric acid (XXIV, n=1)
Trimethylsilyl derivative of
product from reaction 12

m/e	%	m/e	%
73	51	141	1
74	13	143	3
75	12	145	2
76	3	147	47
81	4	148	12
85	2	149	13
105	2	190	5
130	6	191	3
131	100	205	13
132	21	233	13
133	7	234	2
134	2		

2-Hydroxybutyric acid (XXIV, n=1)
Trimethylsilyl derivative of
authentic compound

m/e	%	m/e	%
73	36	147	94
74	5	148	13
75	10	190	14
131	100	205	23
132	24	206	4
133	11	233	19
134	6		

TABLE XXXIX (Continued)

MASS SPECTRA OF α-HYDROXY ACID TRIMETHYLSILYL ESTER-ETHERS

2-Hydroxypentanoic acid (XXIV, n=2)
Trimethylsilyl derivative of
product from reaction 10

m/e	%	m/e	%
73	100	145	87
74	8	146	12
75	16	147	68
77	2	148	7
81	4	157	3
83	3	159	2
103	10	190	6
115	2	219	6
117	2	220	3
129	2	247	7
131	3	248	2
133	10		

2-Hydroxypentanoic acid (XXIV, n=2)
Trimethylsilyl derivative of
authentic compound

m/e	%	m/e	%
72	5	145	100
73	77	146	13
74	9	147	65
75	10	148	15
81	6	149	7
103	4	190	7
129	3	219	10
131	2	220	4
133	4	247	9
		248	1
		249	2

2-Hydroxyhexanoic acid (XXIV, n=3)
Trimethylsilyl derivative of
product from reaction 10

m/e	%	m/e	%
73	100	149	7
74	9	150	2
75	21	159	94
76	3	160	15
103	20	161	5
115	3	190	4
129	4	233	13
131	4	234	2
133	5	235	1
143	2	261	8
147	66	262	1
148	9		

2-Hydroxyhexanoic acid (XXIV, n=3)
Trimethylsilyl derivative of
authentic compound

m/e	%	m/e	%
73	59	149	1
74	2	150	2
75	11	159	100
103	10	160	11
129	2	161	4
131	8	190	5
133	5	233	11
147	45	261	9
148	7	262	1

TABLE XXXIX (Continued)

MASS SPECTRA OF α-HYDROXY ACID TRIMETHYLSILYL ESTER-ETHERS

2-Hydroxyheptanoic acid (XXIV, n=4) product from reaction 10

m/e	%	m/e	%
72	2	101	3
73	49	103	23
74	9	115	2
75	16	117	1
81	2	129	4
83	19	131	4
91	2	133	8
99	1	147	65

2 Hydroxyoctanoic acid (XXIV, n=5) Trimethylsilyl derivative of product from reaction 9

m/e	%	m/e	%
73	83	149	7
74	11	150	3
75	16	157	2
76	3	159	3
77	2	163	2
79	3	172	2
84	3	175	3
87	2	176	2
97	15	187	100
101	7	188	17
102	4	189	4
103	21	190	10
113	2	191	3
117	4	199	3
129	5	200	3
133	5	201	2
134	3	205	2
135	2	261	8
136	4	271	5
143	3	275	3
144	4	289	10
147	49	290	2
148	6		

Trimethylsilyl derivative of

m/e	%	m/e	%
148	13	191	1
149	7	247	13
173	100	248	2
174	21	249	1
175	8	275	10
185	3	276	1
190	4	277	1

2-Hydroxyoctanoic acid (XXIV, n=5) Trimethylsilyl derivative of authentic compound

m/e	%	m/e	%
73	55	133	6
74	6	147	42
75	13	148	11
81	1	149	4
85	1	187	100
97	3	188	18
98	2	189	5
100	4	190	6
103	14	261	13
104	2	289	10
115	2	290	5
129	2	291	2
131	3		

TABLE XXXIX (Continued)

MASS SPECTRA OF α-HYDROXY ACID TRIMETHYLSILYL ESTER-ETHERS

2-Hydroxynonanoic acid (XXIV, n=6) product from reaction 9

m/e	%	m/e	%
73	92	115	5
74	6	116	2
75	19	129	6
83	9	130	5
91	5	131	4
103	34	133	13
109	2	143	4
110	3	147	55
114	3		

2-Hydroxydecanoic acid (XXIV, n=7) Trimethylsilyl derivative of product from reaction 9

m/e	%	m/e	%
73	100	144	8
74	6	147	47
75	30	148	7
77	5	149	11
82	12	155	4
83	24	156	15
103	7	157	5
105	6	172	6
115	5	173	9
116	9	183	10
117	6	199	7
128	7	202	9
129	11	215	43
130	34	216	9
131	8	245	18
132	4	246	9
133	3	275	13
142	17	289	5
143	7	317	5

Trimethylsilyl derivative of

m/e	%	m/e	%
148	9	213	3
149	8	220	3
157	4	245	4
190	3	275	10
191	3	276	7
201	100	289	2
202	23	303	8
203	8	304	2

2-Hydroxydecanoic acid (XXIV, n=7) Trimethylsilyl derivative of authentic compound

m/e	%	m/e	%
72	4	199	5
73	100	201	4
74	10	203	3
75	15	204	3
83	26	215	94
101	4	216	47
103	16	217	16
129	9	228	4
131	5	289	24
133	13	317	19
134	7	318	9
147	77	319	4
148	6	332	1
149	7		

TABLE XL

MASS SPECTRA OF α-HYDROXY DICARBOXYLIC ACID DIMETHYL ESTERS

2-Hydroxynonanedioic acid (XXV, n=6) reaction 2

m/e	%	m/e	%
41	25	67	6
42	6	68	6
43	32	69	32
44	7	74	17
45	10	81	9
55	30	83	7
56	4	85	4
57	13	87	17
58	2	90	11
59	12	95	55

2-Hydroxydecanedioic acid (XXV, n=7) Dimethyl ester of product from reaction 2

m/e	%	m/e	%
41	20	93	5
42	6	95	6
43	19	96	1
44	5	97	5
45	6	98	4
53	5	99	5
55	21	100	1
56	3	101	2
57	16	109	20
59	14	110	4
67	25	111	3
68	3	113	7
69	10	119	3
71	7	125	3
74	19	137	6
79	3	143	3
81	9	155	100
82	4	156	10
83	16	157	3
84	7	158	8
85	2	183	5
87	9	187	19
88	3	188	4
90	5		

Dimethyl ester of product from

m/e	%	m/e	%
96	4	142	9
97	11	144	6
98	7	145	4
99	8	150	3
101	4	151	3
111	7	168	2
113	3	169	5
123	7	171	3
129	8	173	22
141	100	174	2

2-Hydroxydecanedioic acid (XXV, n=7) Dimethyl ester of authentic compound

m/e	%	m/e	%
41	47	93	3
42	8	95	21
43	28	97	5
44	10	98	5
45	9	99	5
53	4	100	6
54	9	101	5
55	64	109	44
57	28	110	5
59	33	111	5
67	50	113	14
68	7	125	8
69	16	136	2
70	4	137	3
71	10	143	5
74	25	145	6
79	5	155	100
81	13	156	18
83	25	157	3
84	9	158	9
85	6	183	5
87	16	187	33
90	18	188	4

TABLE XLI

MASS SPECTRA OF α-HYDROXY DICARBOXYLIC ACID

DIMETHYL ESTER-TRIMETHYLSILYL ETHERS

2-Hydroxyoctanedioic acid (XXV, n=5)
Dimethyl ester-trimethylsilyl ether
of product from reaction 4F

m/e	%	m/e	%
73	100	129	14
74	8	131	6
75	32	133	13
79	7	137	14
81	82	139	8
82	7	155	41
83	7	156	7
89	57	157	6
90	7	159	9
91	9	171	13
99	15	183	20
101	11	187	8
103	7	199	9
105	6	215	18
109	14	231	46
113	16	232	9
115	5	233	4
117	3	259	5
127	64		

2-Hydroxynonanedioic acid (XXV, n=6)
Dimethyl ester-trimethylsilyl ether
of product from reaction 2

m/e	%	m/e	%
41	13	100	4
43	19	101	5
44	14	103	10
45	13	105	11
54	4	123	10
55	12	129	10
56	5	141	50
57	4	142	4
59	21	143	7
60	3	145	7
61	8	151	5
67	5	159	2
68	2	161	3
69	20	162	2
71	4	169	24
72	4	170	7
73	100	200	10
74	13	201	4
75	18	213	8
76	3	229	31
81	12	230	5
85	5	245	98
87	5	246	17
89	23	247	7
90	3	248	2
91	4	261	4
95	71	273	3
96	7	289	1
99	3		

TABLE XLI (Continued)

MASS SPECTRA OF α-HYDROXY DICARBOXYLIC ACID

DIMETHYL ESTER-TRIMETHYLSILYL ETHERS

2-Hydroxydecanedioic acid (XXV, n=7)
Dimethyl ester-trimethylsilyl ether
of product from reaction 2

m/e	%	m/e	%
41	6	109	47
43	13	110	5
45	15	111	5
55	12	119	13
57	9	129	9
59	17	130	5
67	29	131	4
69	7	138	8
71	6	145	9
73	80	155	55
74	9	156	10
75	18	157	4
81	6	159	4
83	10	181	4
85	4	243	19
89	33	244	7
90	5	245	6
95	12	246	2
99	9	259	100
100	6	260	23
101	4	261	2
103	10	275	8
105	7	287	3

2-Hydroxydecanedioic acid (XXV, n=7)
Dimethyl ester-trimethylsilyl ether
of authentic compound

m/e	%	m/e	%
41	27	109	68
42	6	110	7
43	24	111	3
44	6	115	6
45	26	116	4
46	4	117	3
47	4	119	10
53	3	129	20
55	37	130	4
56	4	131	5
57	15	137	12
58	7	145	7
59	64	146	5
60	7	155	62
61	10	156	8
67	38	157	4
68	5	159	15
69	10	161	4
71	10	162	3
72	4	183	7
73	100	185	3
74	26	211	9
75	41	227	8
81	10	229	2
83	16	242	4
85	5	243	58
87	4	244	11
89	5	259	95
90	6	260	41
91	8	261	13
93	6	275	19
95	21	276	5
97	4	287	13
101	12	288	3
103	15	289	4
105	12	303	0.5
107	5	318	0.2

TABLE XLII

MASS SPECTRA OF α-HYDROXY DICARBOXYLIC ACID TRIMETHYLSILYL ESTER-ETHERS

Malic acid (XXV, n=1)
Trimethylsilyl derivative of
product from reaction 12

m/e	%	m/e	%
72	7	191	4
73	100	217	12
74	4	221	4
75	17	229	8
76	4	233	43
77	3	234	7
81	6	235	8
101	3	245	24
116	5	260	5
117	5	261	3
118	7	263	3
129	3	265	10
133	7	305	10
145	3	306	4
147	75	307	9
148	15	309	6
149	6	310	4
175	16	335	29
189	15	336	4
190	20	337	4

Malic acid (XXV, n=1)
Trimethylsilyl derivative of
authentic compound

m/e	%	m/e	%
73	100	189	11
74	9	190	7
75	11	191	10
101	9	192	2
102	2	217	3
117	6	218	4
125	1	221	7
129	1	233	37
130	1	234	5
131	1	235	1
132	1	236	2
133	6	245	13
134	1	246	4
143	4	247	1
145	1	248	3
147	65	263	1
148	5	265	7
149	3	305	1
150	4	306	6
171	3	307	9
175	10	319	5
177	2	335	19
178	1	336	2

TABLE XLII (Continued)

MASS SPECTRA OF α-HYDROXY DICARBOXYLIC ACID TRIMETHYLSILYL ESTER-ETHERS

2-Hydroxypentanedioic acid (XXV, n=2) Trimethylsilyl derivative of product from reaction 12

m/e	%	m/e	%
73	61	204	5
75	22	205	3
77	5	215	4
85	19	219	5
99	5	221	5
101	8	232	5
113	4	247	100
115	5	248	23
117	5	249	9
129	50	250	6
131	7	259	6
132	5	261	4
133	4	275	7
147	67	295	8
148	5	321	9
149	20	349	39
157	24	350	14
160	5	351	6
203	8		

2-Hydroxyhexanedioic acid (XXV, n=3) product from reaction 12

m/e	%	m/e	%
73	41	143	4
74	11	144	4
75	32	147	41
85	7	148	7
99	6	149	11
101	3	154	3
109	16	155	5
129	48	157	7
133	6	171	64
139	6	172	6
142	3		

2-Hydroxypentanedioic acid (XXV, n=2) Trimethylsilyl derivative of authentic compound

m/e	%	m/e	%
71	3	158	4
72	6	163	5
73	39	203	30
75	13	204	9
77	3	218	2
85	9	219	4
101	3	220	2
116	8	221	4
129	73	231	9
130	9	232	16
131	4	233	5
133	7	247	100
134	3	248	13
147	52	349	49
148	6	350	7
149	6	351	11
157	11		

Trimethylsilyl derivative of

m/e	%	m/e	%
173	4	245	16
179	4	261	100
188	4	262	23
191	4	263	12
199	3	264	6
203	26	301	6
204	4	335	4
205	4	363	55
207	9	364	26
217	9	365	7

TABLE XLII (Continued)

MASS SPECTRA OF α-HYDROXY DICARBOXYLIC ACID TRIMETHYLSILYL ESTER-ETHERS

2-Hydroxyheptanedioic acid (XXV, n=4) Trimethylsilyl derivative of product from reaction 12

m/e	%	m/e	%
71	53	158	11
72	11	159	10
73	100	169	47
74	30	170	4
75	82	171	5
77	12	185	100
81	5	186	27
83	8	187	7
85	6	191	16
91	4	204	5
95	23	213	8
97	8	217	7
99	3	218	4
101	7	219	3
103	15	220	5
105	4	221	7
111	3	231	7
113	9	232	1
115	8	233	3
116	6	243	4
117	11	244	3
119	7	245	7
123	24	258	3
129	14	259	22
130	10	260	2
131	14	274	4
133	24	275	100
134	5	276	26
141	15	277	10
142	14	287	11
145	8	303	5
147	100	349	9
153	6	377	37
155	9	378	8
157	54	379	4

2-Hydroxyheptanedioic acid (XXV, n=4) Trimethylsilyl derivative of product from reaction 10

m/e	%	m/e	%
73	100	151	6
74	6	157	16
75	64	158	4
81	9	159	5
83	11	168	4
85	6	169	14
93	5	171	6
94	5	173	4
95	6	185	40
101	7	186	12
105	7	187	5
107	5	215	8
113	13	219	10
117	11	245	9
121	4	259	6
123	10	260	9
129	10	275	38
133	5	276	12
134	5	277	8
137	8	287	3
138	7	288	3
139	5	289	3
141	4	303	7
142	4	349	5
145	4	377	14
147	73	378	9
148	12	379	3
149	12		

TABLE XLII (Continued)

MASS SPECTRA OF α-HYDROXY DICARBOXYLIC ACID TRIMETHYLSILYL ESTER-ETHERS

2-Hydroxyoctanedioic acid (XXV, n=5)
Trimethylsilyl derivative of product from reaction 10

m/e	%	m/e	%
73	78	149	11
74	8	171	50
75	40	172	9
79	6	183	31
81	37	199	46
127	11	289	100
129	12	290	23
131	6	291	13
133	11	363	8
137	24	391	23
147	54	392	5
148	18	393	3

2-Hydroxynonanedioic acid (XXV, n=6)
Trimethylsilyl derivative of product from reaction 10

m/e	%	m/e	%
73	84	171	2
74	15	185	5
75	39	186	1
76	3	190	2
77	3	191	2
79	4	197	7
81	8	199	2
95	39	203	1
96	4	204	2
97	2	213	21
101	3	214	4
103	4	215	3
105	2	217	4
115	1	220	2
116	3	221	2
117	5	225	1
123	20	241	3
124	3	269	2
129	13	287	9
130	2	288	4
131	4	290	2
133	9	303	100
141	8	304	32
143	2	305	11
145	1	306	2
147	60	307	1
148	8	315	2
149	10	377	9
150	2	378	3
151	23	379	3
152	3	405	11
169	3	406	3
170	3	407	1

TABLE XLII (Continued)

MASS SPECTRA OF α-HYDROXY DICARBOXYLIC ACID TRIMETHYLSILYL ESTER-ETHERS

2-Hydroxydecanedioic acid (XXV, n=7) Trimethylsilyl derivative of product from reaction 10

m/e	%	m/e	%
73	84	143	3
74	6	147	39
75	28	148	5
76	1	149	5
77	1	155	9
79	1	165	8
81	2	203	1
83	2	204	1
91	2	211	4
93	4	223	3
95	9	227	5
101	2	228	2
103	3	229	1
105	1	301	8
107	1	302	2
109	20	303	5
110	3	317	100
115	1	318	30
117	4	319	15
119	10	329	3
120	2	391	11
121	2	392	5
129	11	393	2
131	5	419	9
133	8	420	2
137	14	421	2

2-Hydroxydecanedioic acid (XXV, n=7) Trimethylsilyl derivative of authentic compound

m/e	%	m/e	%
72	2	169	1
73	65	175	2
74	6	177	2
75	24	183	1
76	4	185	1
77	2	189	1
79	3	190	2
81	3	199	2
91	2	203	2
93	3	204	3
95	7	211	5
99	2	217	4
101	3	219	2
103	1	220	2
105	2	221	2
107	2	226	1
109	17	227	7
110	2	228	3
116	2	229	1
117	3	255	3
119	8	273	2
121	2	301	11
123	2	302	2
129	16	303	2
130	3	317	100
131	4	318	35
132	1	319	15
133	6	320	4
136	2	329	3
137	13	391	19
138	1	392	5
147	39	393	2
148	8	419	7
149	10	420	2
155	11	421	2
156	2	434	0.4
165	9		

TABLE XLIII

MASS SPECTRA OF ω-HYDROXY ACID TRIMETHYLSILYL ESTER-ETHERS

7-Hydroxyheptanoic acid (XXII, n=5)
Trimethylsilyl derivative of
product from reaction 23F

m/e	%	m/e	%
72	5	133	10
73	90	143	12
74	15	147	100
75	85	148	10
76	25	149	45
83	30	158	5
85	7	165	7
88	8	183	6
93	7	185	45
95	5	186	7
101	7	203	15
102	4	204	11
103	5	210	15
111	13	211	8
112	7	218	11
113	5	259	17
115	14	260	6
127	7	275	70
131	7	276	10
132	7	277	12

9-Hydroxynonanoic acid (XXII, n=7)
authentic compound

m/e	%	m/e	%
73	48	95	6
74	11	97	3
75	43	103	13
76	7	111	3
77	7	117	18
79	8	118	3
81	6	121	9
83	3	128	3
93	6	129	12

8-Hydroxyoctanoic acid (XXII, n=6)
Trimethylsilyl derivative of
product from reaction 23F

m/e	%	m/e	%
73	100	119	5
74	9	124	5
75	68	125	8
76	6	129	20
77	5	131	8
79	7	132	11
81	14	133	4
82	5	134	5
83	18	137	8
89	5	145	6
95	5	147	80
96	3	148	25
97	8	149	25
99	5	150	2
101	10	152	3
103	15	199	33
104	6	200	9
107	5	273	8
111	3	279	5
113	3	286	7
115	6	289	55
116	4	290	9
117	13	291	8

Trimethylsilyl derivative of

m/e	%	m/e	%
132	6	204	6
133	3	205	3
138	11	213	36
139	10	217	4
147	38	227	6
148	20	287	24
149	21	303	100
171	3	304	21
		305	11

TABLE XLIV

MASS SPECTRA OF 9,10-DIHYDROXYSTEARIC ACID TRIMETHYLSILYL ESTER-ETHER

9,10-Dihydroxystearic acid (VII), low melting isomer. Trimethylsilyl derivative of product from reaction 9. First peak of doublet.

m/e	%	m/e	%
73	67	206	8
74	10	214	20
75	11	215	52
83	19	216	8
103	10	217	8
109	7	227	17
129	14	317	100
132	11	318	48
133	9	319	22
137	7	329	19
143	7	390	25
147	23	391	19
148	14	392	10
149	6	517	21
191	16	518	8
204	18	519	8
205	8		

9,10-Dihydroxystearic acid (VII), low melting isomer. Trimethylsilyl derivative of authentic compound

m/e	%	m/e	%
73	48	161	1
74	2	187	1
75	16	203	2
77	2	204	9
81	4	205	3
83	5	214	6
93	2	215	76
95	4	216	14
101	3	217	12
103	11	218	4
107	1	219	2
109	6	227	5
115	2	301	4
117	2	317	100
121	1	318	31
129	13	319	15
130	3	320	2
131	4	329	2
133	3	330	1
135	2	390	19
136	4	391	15
143	2	392	6
145	1	393	2
147	22	427	2
148	3	517	12
149	5	518	6
150	1	519	2
155	4	520	1
157	1	532	0.5

TABLE XLIV (Continued)

MASS SPECTRA OF 9,10-DIHYDROXYSTEARIC ACID TRIMETHYLSILYL ESTER-ETHER

9,10-Dihydroxystearic acid (VII), high melting isomer. Trimethylsilyl derivative of product from reaction 9. Second peak of doublet

m/e	%	m/e	%
72	5	181	4
73	100	185	6
74	15	187	4
75	29	204	8
83	10	214	5
95	6	215	79
101	4	216	10
102	4	217	10
103	18	227	5
109	14	228	5
129	8	229	4
131	9	316	7
133	7	317	96
137	8	318	25
143	3	319	17
144	3	320	3
147	29	390	10
148	6	391	17
149	15	392	8
150	5	393	6
151	3	426	5
155	13	517	11
167	8	518	4
179	4		

9,10-Dihydroxystearic acid (VII), high melting isomer. Trimethylsilyl derivative of authentic compound

m/e	%	m/e	%
71	3	151	1
73	75	155	6
74	8	184	1
75	20	185	2
76	1	186	1
77	1	204	11
81	4	205	3
83	7	206	1
91	3	214	6
93	4	215	85
95	4	216	12
97	2	217	13
101	3	218	3
103	7	226	2
105	1	227	4
107	1	301	4
108	2	302	2
109	9	303	2
110	1	316	4
115	2	317	100
116	2	318	31
117	4	319	13
119	2	320	3
121	2	329	2
127	1	390	19
129	14	391	15
130	5	392	4
131	2	393	2
133	4	427	2
137	3	428	1
141	3	517	12
143	3	518	7
147	17	519	4
148	4	532	0.2
149	4		

TABLE XLV

MASS SPECTRA OF TRIHYDROXYOCTADECENOIC ACID TRIMETHYLSILYL ESTER-ETHERS

Trihydroxyoctadecenoic acid (XI) First peak of doublet, trimethylsilyl derivative, reaction 10

m/e	%	m/e	%
73	100	231	4
74	13	239	7
75	53	240	3
81	3	241	5
83	4	259	6
93	4	275	9
101	7	301	5
103	6	317	74
107	9	318	26
109	16	319	6
113	4	329	74
119	6	330	2
121	4	331	11
129	17	343	7
147	33	390	17
149	6	416	7
155	7	417	7
157	4	419	33
159	5	420	9
173	32	421	6
174	6	428	6
185	7	503	3
199	36	513	4
200	8	514	4
203	5	515	2
204	7	518	15
211	11	519	8
212	4	520	4
217	5	603	2
227	6		

Trihydroxyoctadecenoic acid (XI) Second peak of doublet, trimethylsilyl derivative, reaction 10

m/e	%	m/e	%
73	100	200	5
74	18	201	4
75	37	203	4
81	3	204	8
83	5	211	9
91	4	212	8
93	6	213	3
95	10	217	11
96	5	227	7
101	4	230	8
103	9	231	5
105	5	243	3
107	7	275	43
109	15	276	12
111	3	277	4
113	3	287	4
116	5	301	7
117	8	303	3
119	5	317	67
120	3	318	22
121	5	319	15
129	33	329	43
130	5	330	11
131	9	331	5
133	4	343	18
135	3	344	5
137	6	345	3
139	3	355	3
143	4	356	4
145	4	390	9
146	13	391	4
147	38	416	16
149	8	417	7
155	17	419	19
156	5	420	3
157	4	421	3
159	2	439	7
163	4	503	3
173	80	504	4
174	12	513	5
175	6	515	3
182	5	518	20
185	16	519	12
187	4	520	6
188	3	603	2
199	29	618	0.3

TABLE XLVI

MASS SPECTRA OF ω-ACETO ACID METHYL ESTERS

5-Oxohexanoic acid (XXVI, n=3)
Methyl ester of authentic compound

m/e	%	m/e	%
41	7	84	11
42	25	85	24
43	100	87	12
44	6	97	3
55	22	101	10
56	3	102	4
58	5	112	24
59	15	113	20
71	5	129	1
74	36	144	2

8-Oxononanoic acid (XXVI, n=6)
Methyl ester of product from reaction 2

m/e	%	m/e	%
41	12	85	2
42	6	87	25
43	100	88	7
44	4	93	2
45	4	97	46
48	2	98	1
55	15	99	3
57	5	109	11
58	34	111	9
59	13	113	7
67	3	126	6
68	3	129	36
69	26	130	3
70	4	131	2
71	3	139	5
73	3	140	2
74	13	143	2
75	4	144	1
81	3	154	2
83	7	155	3
84	3	156	1

7-Oxooctanoic acid (XXVI, n=5)
Methyl ester of product from reaction 5

m/e	%	m/e	%
41	72	93	1
42	79	94	3
43	100	95	41
44	30	96	9
45	21	97	26
47	1	98	27
48	3	99	16
49	4	100	5
50	3	101	12
51	5	102	4
52	2	107	8
53	10	108	2
54	9	109	2
55	98	111	9
56	15	112	14
57	14	113	7
58	57	114	21
59	58	115	67
60	3	116	11
61	2	117	1
63	3	119	1
65	1	120	10
67	17	122	7
68	6	123	13
69	66	124	6
70	18	125	22
71	30	126	1
72	2	127	4
73	40	128	6
74	48	129	7
75	3	130	6
76	3	140	17
79	3	141	15
80	3	142	2
81	8	145	2
82	4	154	3
83	48	155	2
84	18	156	4
85	9	157	7
87	59	158	1
88	10	172	2

TABLE XLVI (Continued)

MASS SPECTRA OF ω-ACETO ACID METHYL ESTERS

8-Oxononanoic acid (XXVI, n=6)
Methyl ester of product from reaction 5

m/e	%	m/e	%
41	75	87	70
42	59	88	9
43	84	94	7
44	35	95	6
45	32	96	6
51	6	97	64
53	15	98	7
54	14	100	7
55	100	101	16
56	27	109	31
57	21	110	9
58	64	111	18
59	68	112	4
60	6	113	16
67	20	115	10
68	33	126	9
69	76	127	4
70	12	128	27
71	35	129	64
72	5	130	13
73	16	138	3
74	68	139	5
75	14	141	2
77	5	143	4
79	6	144	4
81	8	154	7
82	11	155	11
83	49	156	4
84	14	171	5
85	13	186	1

9-Oxodecanoic acid (XXVI, n=7)
Methyl ester of product from reaction 5

m/e	%	m/e	%
41	24	97	10
42	9	98	14
43	100	99	7
44	6	101	10
45	9	102	1
53	3	109	3
54	3	110	12
55	56	111	58
56	6	112	5
57	8	113	5
58	32	114	2
59	24	115	8
67	7	123	6
68	9	124	7
69	17	125	12
70	1	126	4
71	15	127	5
72	3	130	3
74	46	140	5
75	5	142	9
79	3	143	50
80	4	144	8
81	4	145	2
82	10	149	2
83	43	150	1
84	7	151	2
85	20	157	4
87	36	168	5
88	7	169	15
95	3	185	1
96	10	200	2

TABLE XLVI (Continued)

MASS SPECTRA OF ω-ACETO ACID METHYL ESTERS

9-Oxodecanoic acid (XXVI, n=7)

m/e	%	m/e	%
41	13	67	3
42	4	68	4
43	100	69	23
44	5	70	4
53	2	71	14
54	2	73	2
55	43	74	12
56	6	81	8
57	2	82	4
58	47	83	28
59	12	84	4

17-Oxooctadecanoic acid (XXVI, n=15)
published by Ryhage and Stenhagen (68)

m/e	%	m/e	%
41	42	85	14
42	11	87	42
43	100	88	4
44	5	93	4
45	4	94	3
53	5	95	19
55	58	96	12
56	9	97	29
57	25	98	33
58	73	99	6
59	37	100	3
67	17	101	6
68	7	107	4
69	48	108	2
70	7	109	11
71	42	110	4
72	3	111	13
73	51	112	3
74	44	113	2
75	7	115	3
79	4	121	6
80	3	122	2
81	20	123	7
82	9	124	3
83	40	125	10
84	21	126	3
		127	2

Methyl ester of product from reaction 2

m/e	%	m/e	%
87	18	127	4
95	2	134	4
97	2	142	6
98	5	143	24
101	3	144	4
111	38	168	3
112	5	169	7
113	2	185	2
115	3	186	1
125	5	200	0.1

Methyl ester, spectrum

m/e	%	m/e	%
135	7	213	3
137	4	219	3
141	3	220	2
143	5	221	3
153	3	222	53
157	2	223	82
163	3	224	14
167	6	225	3
168	4	227	4
171	3	237	7
178	4	238	7
179	3	239	11
180	9	240	2
181	9	242	4
182	10	252	3
183	3	254	15
185	5	255	53
194	3	256	9
195	3	262	2
196	3	270	3
199	6	280	10
204	6	281	20
205	37	282	4
206	6	297	3
211	2	312	9
		313	4

TABLE XLVII

MASS SPECTRUM OF A BOROHYDRIDE REDUCED ω-ACETO ACID METHYL ESTER

9-Hydroxydecanoic acid, borohydride reduction product of 9-oxodecanoic acid (XXVI, n=7). Methyl ester-trimethylsilyl ether

m/e	%	m/e	%	m/e	%	m/e	%
41	12	75	30	97	2	119	6
43	10	79	2	99	2	135	2
45	8	81	3	101	3	146	10
47	6	83	8	103	3	159	9
55	22	85	2	105	2	227	8
57	4	87	4	107	6	230	12
59	6	89	7	109	3	231	3
61	6	91	3	110	2	233	1
69	15	93	1	117	100	243	3
73	76	95	2	118	16	259	8
74	16						

TABLE XLVIII

MASS SPECTRA OF γ-KETO ACID METHYL ESTERS

4-Oxoheptanoic acid (XXVII, n=2)
Methyl ester of product from reaction 2

m/e	%	m/e	%
41	17	99	6
42	6	101	6
43	100	109	5
44	14	111	7
45	9	112	3
55	38	113	4
56	10	115	99
57	11	116	4
59	15	127	35
71	88	128	6
87	19	130	38
97	4	132	3
98	19	133	2

4-Oxononanoic acid (XXVII, n=4)
Methyl ester of product from reaction 2

m/e	%	m/e	%
41	20	89	2
42	16	98	100
43	97	99	47
44	6	100	4
45	3	109	4
55	41	111	17
56	17	112	5
57	8	114	3
58	7	115	77
59	22	130	52
71	45	131	4
74	9	143	6
81	4	152	4
82	4	153	2
83	2	154	2
85	4	155	19
87	21	156	4
88	5	169	3

4-Oxooctanoic acid (XXVII, n=3)
Methyl ester of product from reaction 2

m/e	%	m/e	%
41	42	85	79
42	9	87	18
43	24	98	71
44	11	99	4
45	3	109	3
55	71	111	24
56	26	112	5
57	100	114	3
58	5	115	91
59	31	116	2
69	7	130	61
70	10	131	10
71	9	132	3
74	10	141	22
83	7	143	5

4-Oxooctadecanoic acid (XXVII, n=13)
Methyl ester, spectrum published by Ryhage and Stenhagen (68)

m/e	%	m/e	%
41	6	99	6
42	1	109	2
43	10	111	11
55	9	112	2
56	2	115	21
57	10	116	1
59	2	123	1
67	2	125	2
69	4	130	100
70	2	131	10
71	6	143	8
81	2	225	15
83	3	226	3
85	5	280	3
87	3	281	12
95	3	282	3
97	2	312	4
98	38	313	1

TABLE XLIX

MASS SPECTRA OF γ,β-DIHYDROXY ACID TRIMETHYLSILYL ESTER-ETHERS

2,3-Dihydroxyheptanoic acid (XXVIII, n=3) Trimethylsilyl derivative of product from reaction 10

m/e	%	m/e	%
72	3	147	34
73	100	148	6
74	13	149	5
75	34	159	47
81	7	160	4
84	2	171	10
89	4	174	3
102	9	178	2
103	15	207	4
104	4	220	8
117	3	261	3
129	6	292	19
131	4	293	6
133	9	294	3

2,3-Dihydroxyoctanoic acid (XXVIII, n=4) Trimethylsilyl derivative of product from reaction 10

m/e	%	m/e	%
73	100	157	1
74	11	159	1
75	13	173	32
77	5	174	10
81	1	175	6
83	6	176	2
89	3	177	3
91	2	185	1
94	4	187	1
99	1	191	2
100	1	201	1
101	3	203	1
102	3	205	2
103	14	207	1
105	9	217	2
111	3	220	2
115	3	221	3
116	1	233	8
117	6	247	4
129	3	248	3
130	5	249	2
131	2	257	2
133	3	259	2
147	21	292	24
148	3	293	10
149	2	294	3
151	2	377	6

TABLE L

MASS SPECTRA OF β,γ-DIHYDROXY ACID TRIMETHYLSILYL ESTER-ETHERS

3,4-Dihydroxypentanoic acid (XXIX, n=0) Trimethylsilyl derivative of product from reaction 12

m/e	%	m/e	%
101	19	205	3
102	4	206	3
103	7	207	4
115	7	217	11
116	16	218	5
117	27	219	8
129	12	221	32
130	4	222	13
131	8	233	43
132	3	234	11
133	36	235	5
134	6	236	3
143	4	237	5
145	4	245	15
147	100	261	7
148	39	262	1
149	21	263	2
159	5	275	1
163	8	279	4
171	17	306	33
172	7	307	28
173	9	308	12
174	7	309	8
175	11	335	16
177	3	336	3
191	4	337	4
204	3		

3,4-Dihydroxynonanoic acid (XXIX, n=4) Trimethylsilyl derivative of product from reaction 10

m/e	%	m/e	%
72	1	150	5
73	100	154	3
74	16	155	13
75	73	159	4
76	9	171	3
77	3	172	3
79	2	173	85
81	4	174	14
83	8	175	4
85	1	185	2
87	2	187	2
93	1	189	2
95	4	190	9
97	4	191	1
101	3	193	2
102	1	199	1
103	17	201	1
107	1	211	2
109	1	215	1
111	2	217	11
114	2	218	3
115	2	220	1
116	3	221	2
117	3	233	2
124	2	245	5
125	7	247	5
127	1	248	6
128	2	271	1
129	4	273	3
130	1	275	4
131	4	289	6
132	1	293	2
133	6	301	8
134	3	305	3
135	5	306	20
137	1	307	12
147	47	308	1
148	9	391	1
149	15	393	2

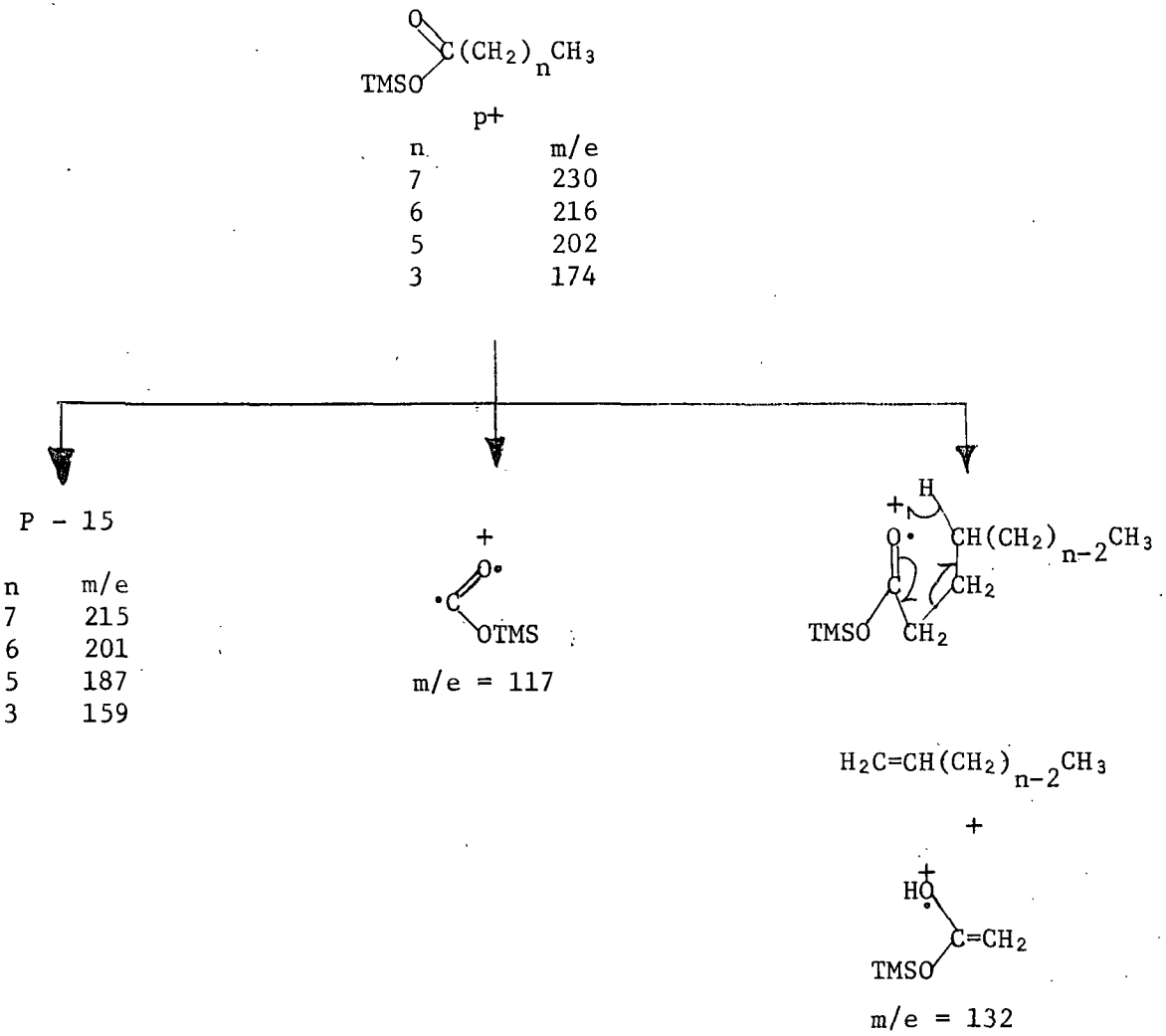


Figure 30. Fragmentation Pattern for Mass Spectra of Monocarboxylic Acid Trimethylsilyl Esters

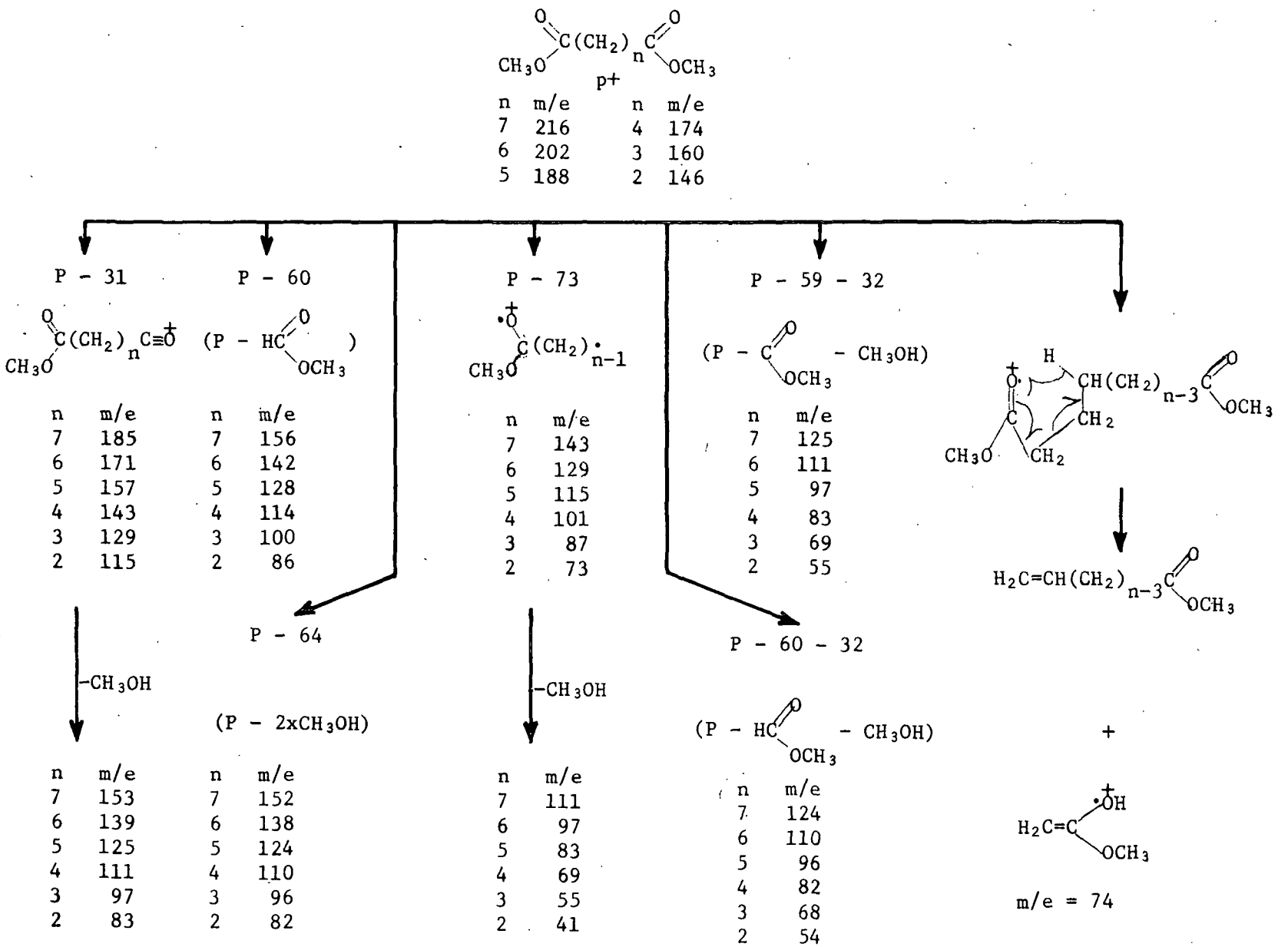


Figure 31. Fragmentation Pattern for Mass Spectra of Dicarboxylic Acid Dimethyl Esters

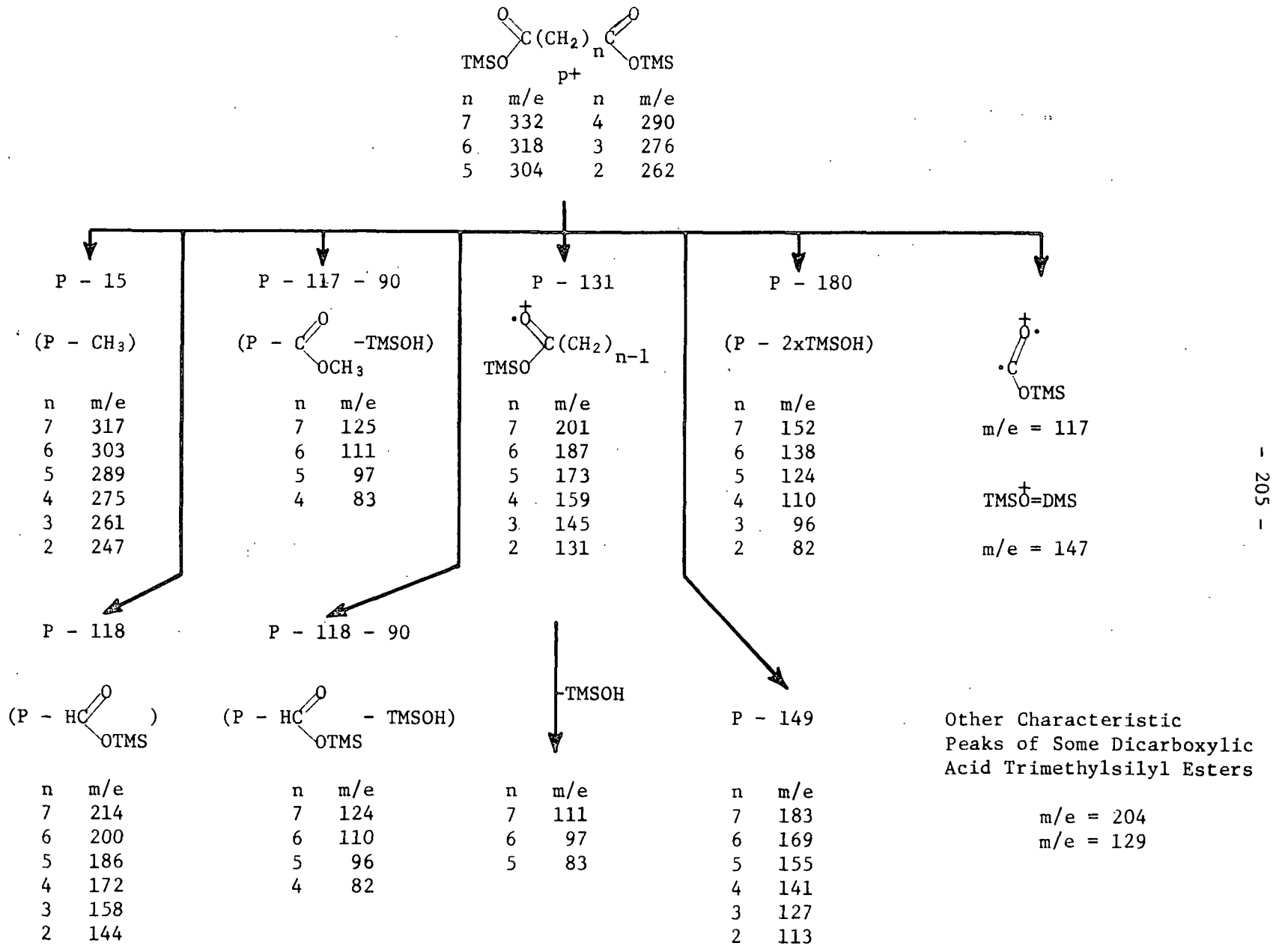


Figure 32. Fragmentation Pattern for Mass Spectra of Dicarboxylic Acid Ditrimethylsilyl Esters.

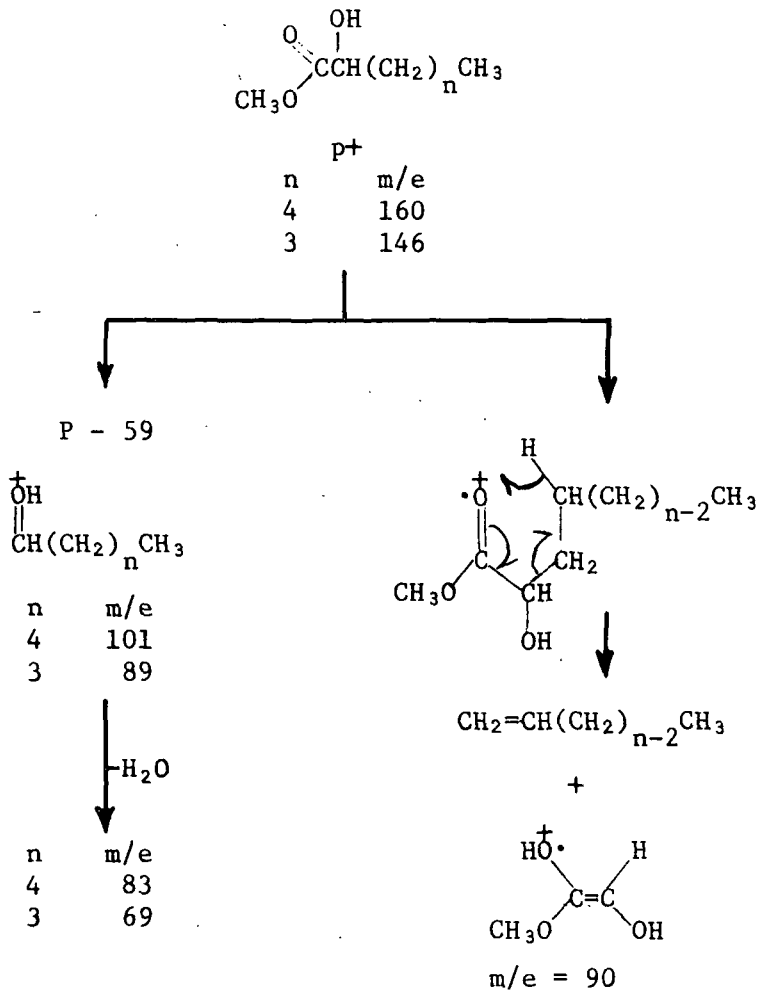


Figure 33. Fragmentation Pattern for Mass Spectra of α-Hydroxy Acid Methyl Esters

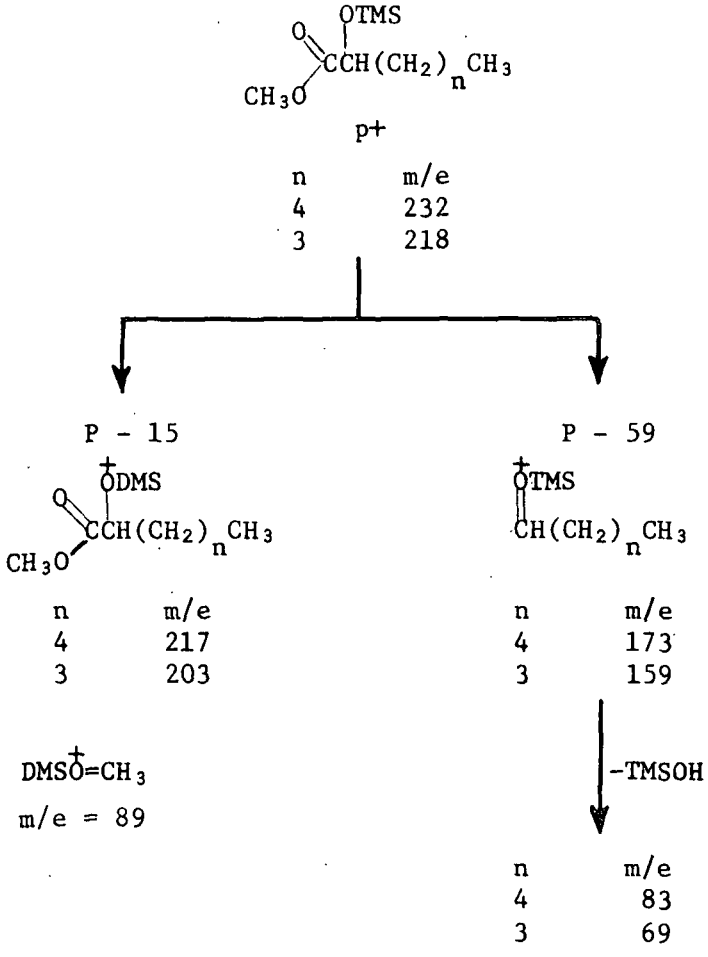


Figure 34. Fragmentation Pattern for Mass Spectra of α-Hydroxy Acid Methyl Ester-trimethylsilyl Ethers

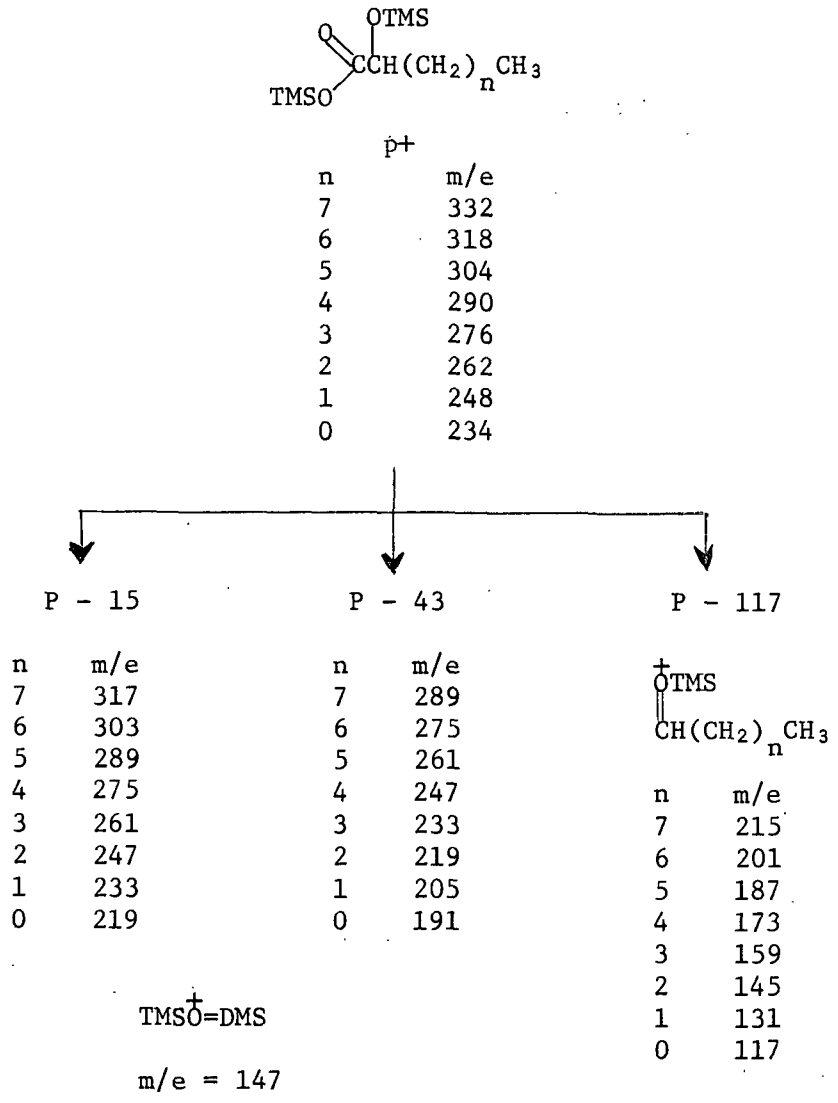


Figure 35. Fragmentation Pattern for Mass Spectra of α-Hydroxy Acid Trimethylsilyl Ester-Ethers

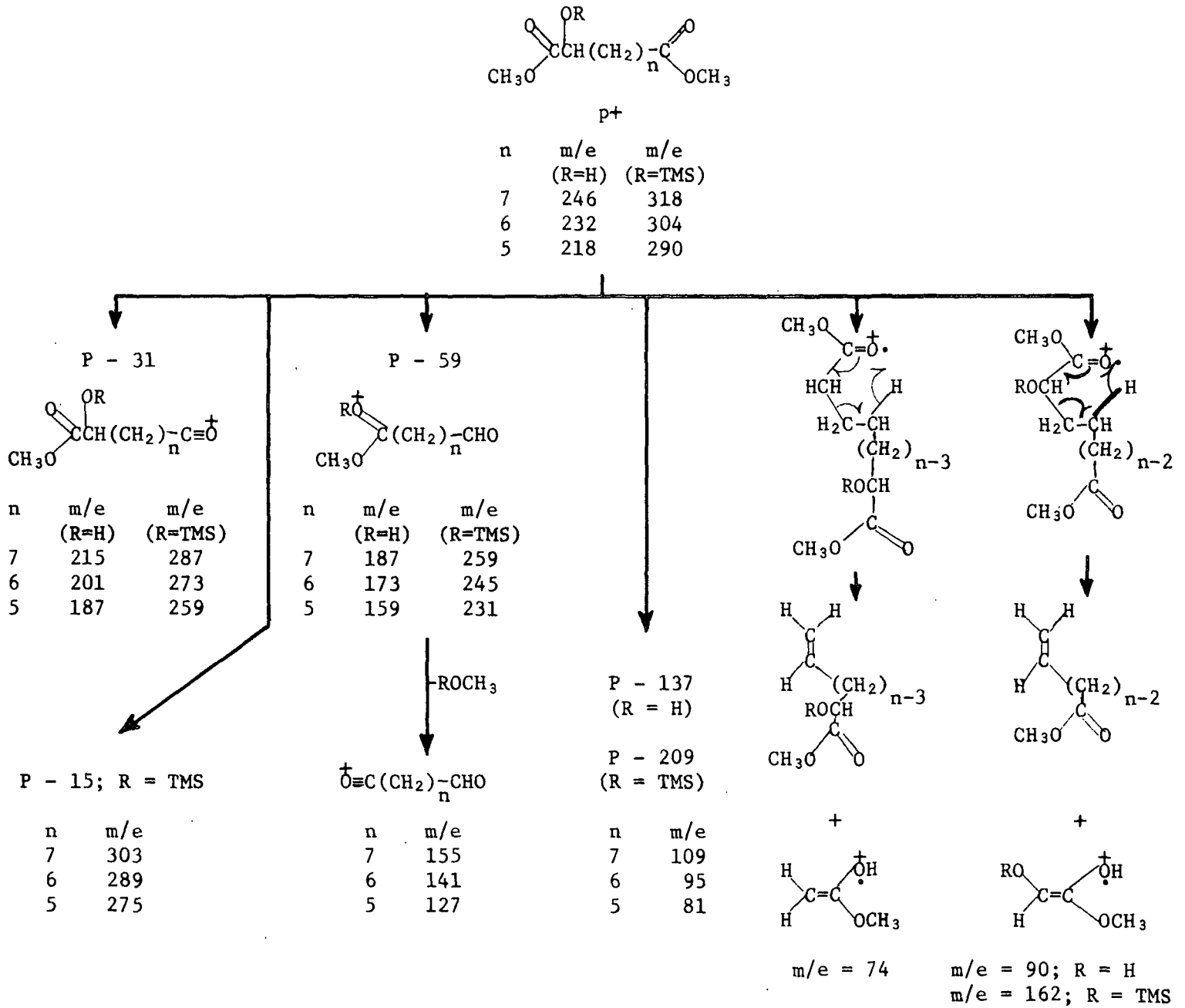


Figure 36. Fragmentation Pattern for Mass Spectra of α-Hydroxy Dicarboxylic Acid Dimethyl Esters and Dimethyl Ester-Trimethylsilyl Ethers

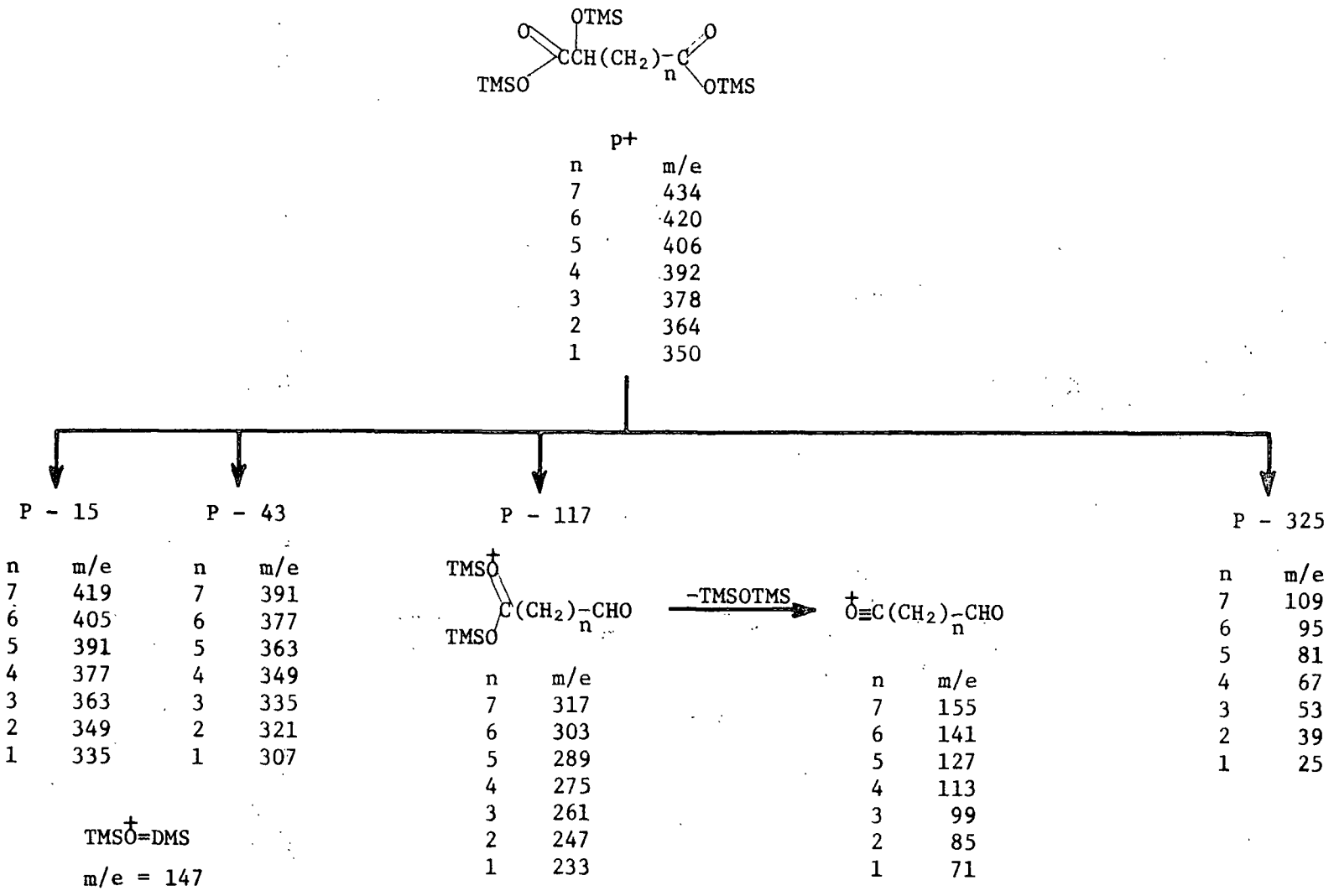


Figure 37. Fragmentation Pattern for Mass Spectra of α-Hydroxy Dicarboxylic Acid Trimethylsilyl Ester-Ethers

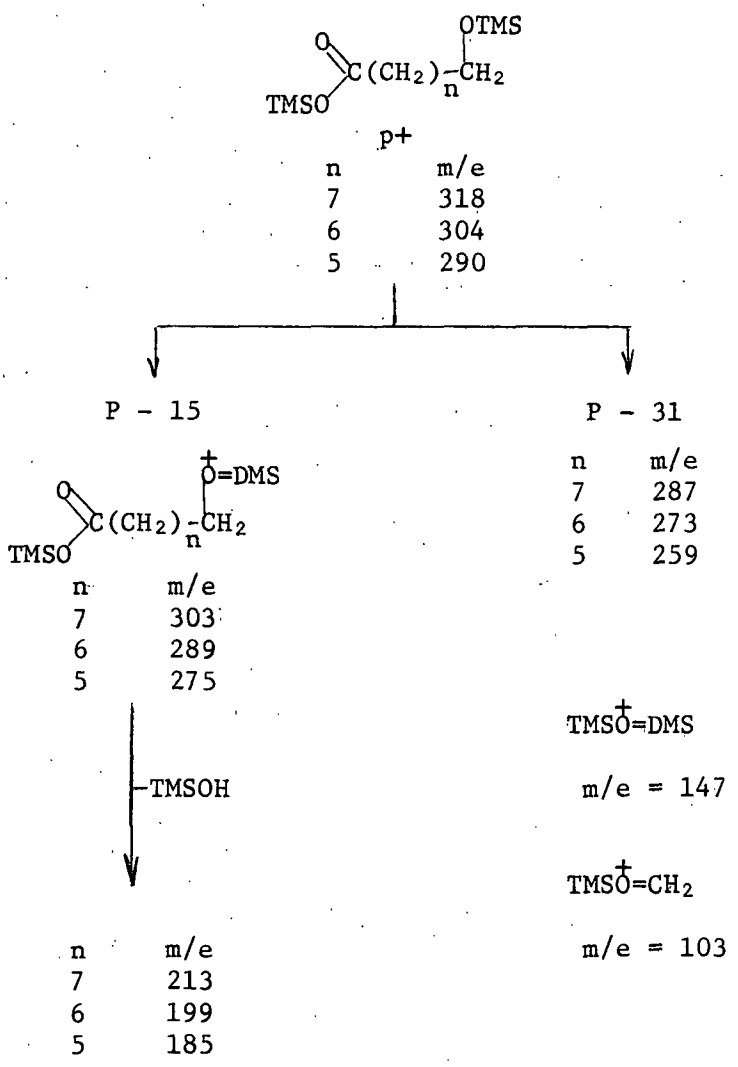


Figure 38. Fragmentation Pattern for Mass Spectra of ω-Hydroxy Acid Trimethylsilyl Ester-Ethers

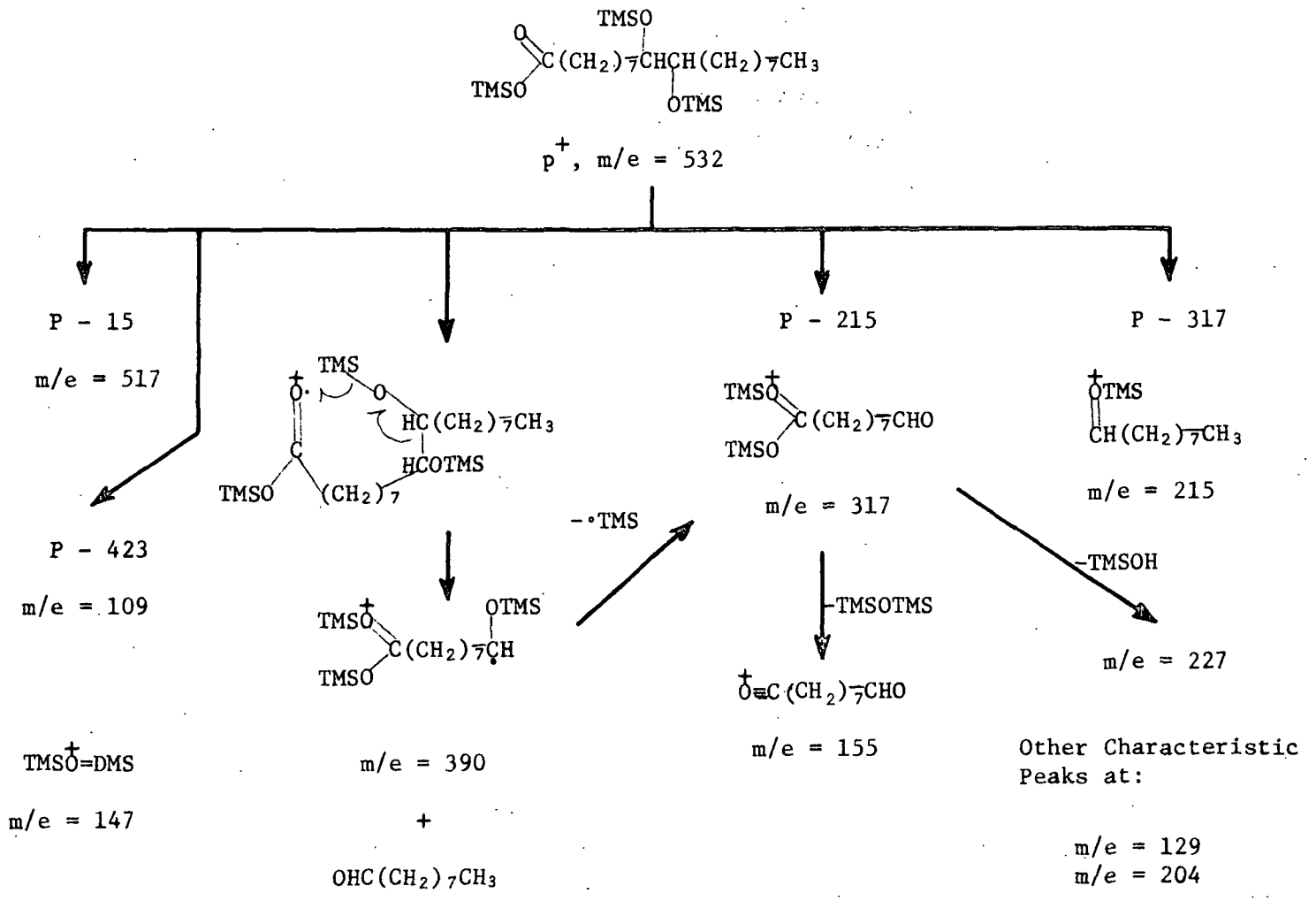


Figure 39. Fragmentation Pattern for Mass Spectrum of 9,10-Dihydroxystearic Acid as Trimethylsilyl Ester-Ether.

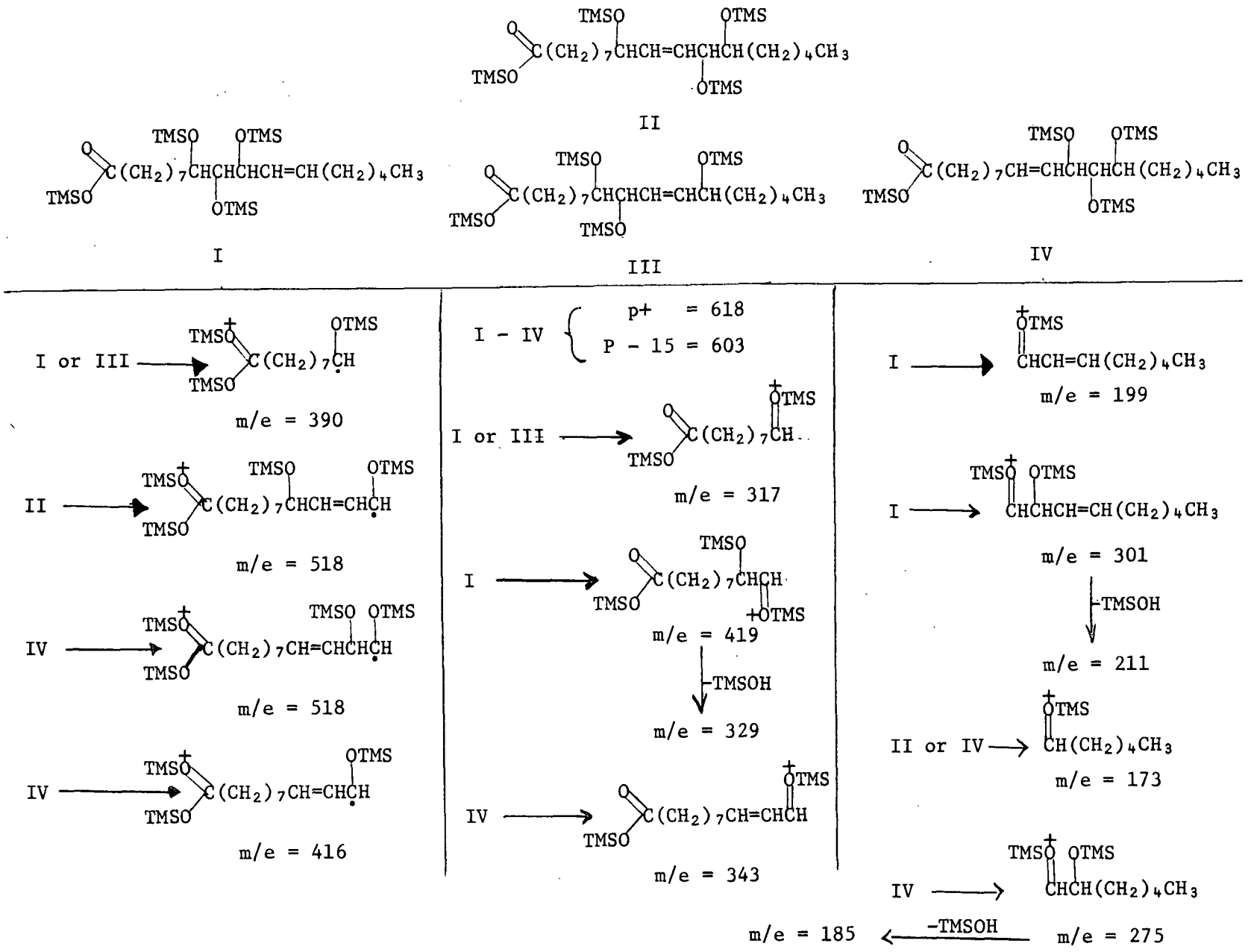


Figure 40. Fragmentation Pattern for Mass Spectra of Trihydroxyoctadecenoic Acid Trimethylsilyl Ester-Ethers

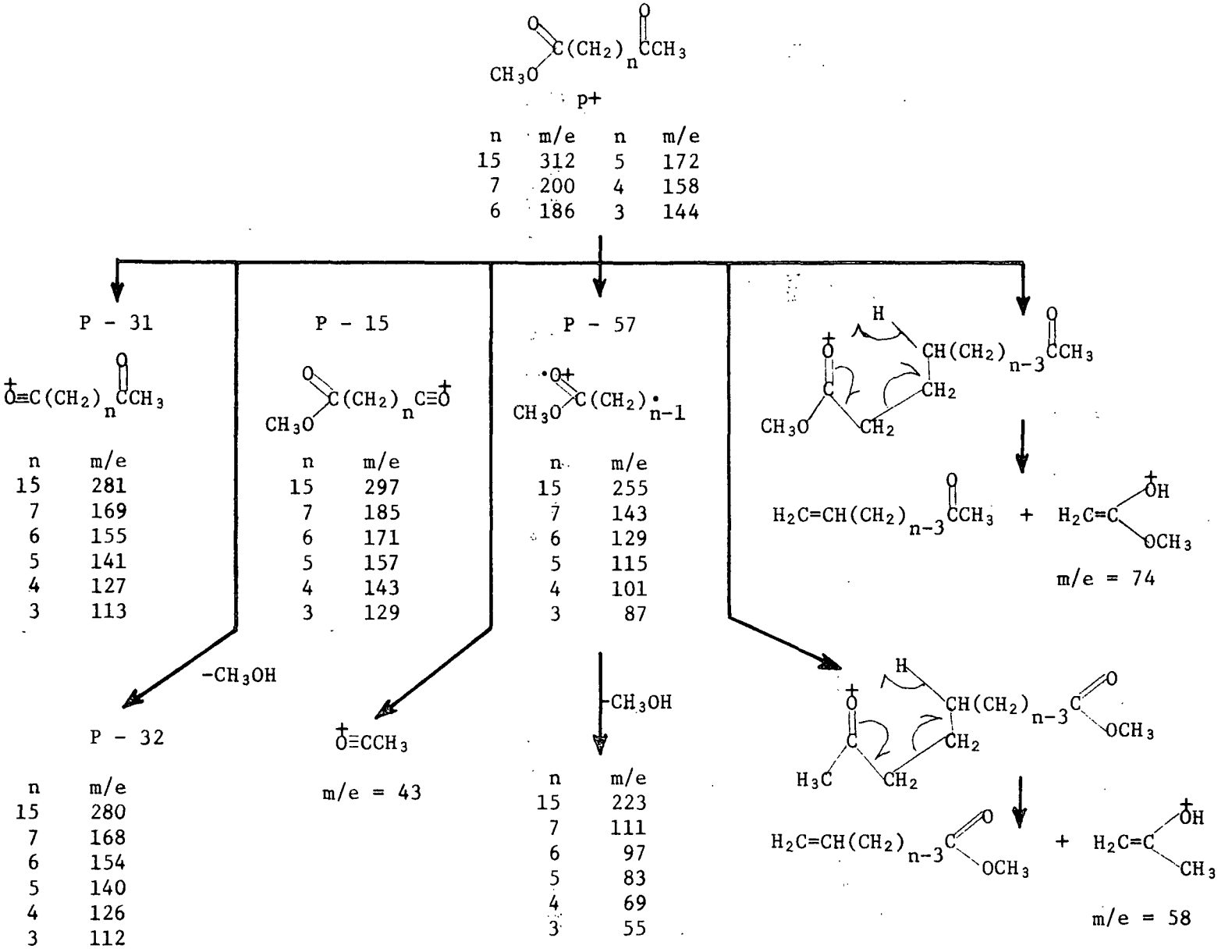


Figure 41. Fragmentation Pattern for Mass Spectra of ω-Aceto Acid Methyl Esters

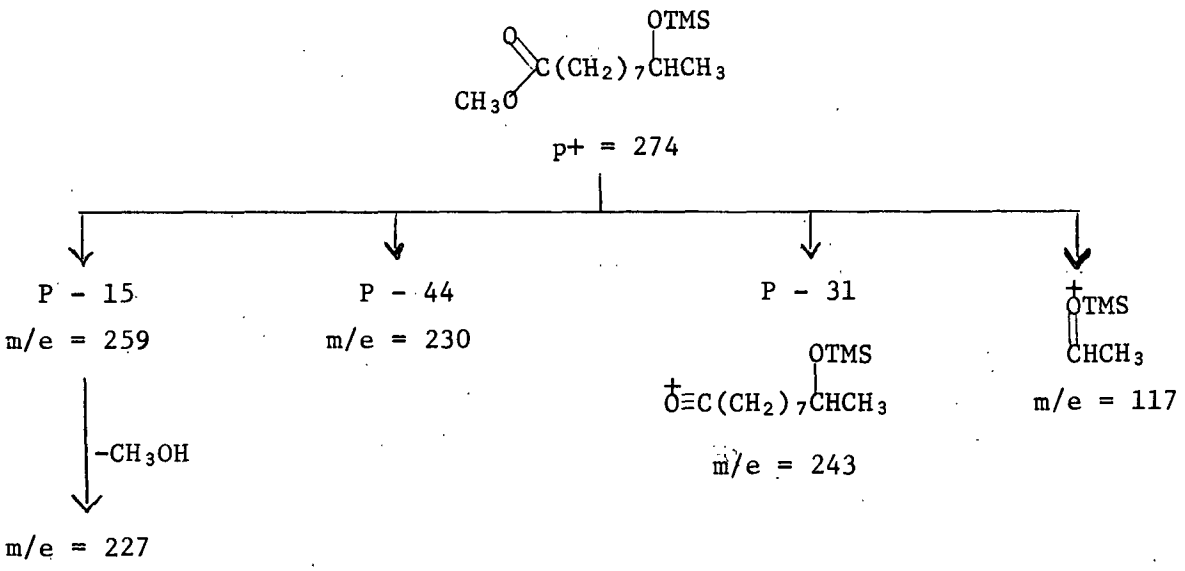


Figure 42. Fragmentation Pattern for Mass Spectrum of Borohydride Reduced 9-Oxodecanoic Acid as its Methyl Ester-Trimethylsilyl Ether

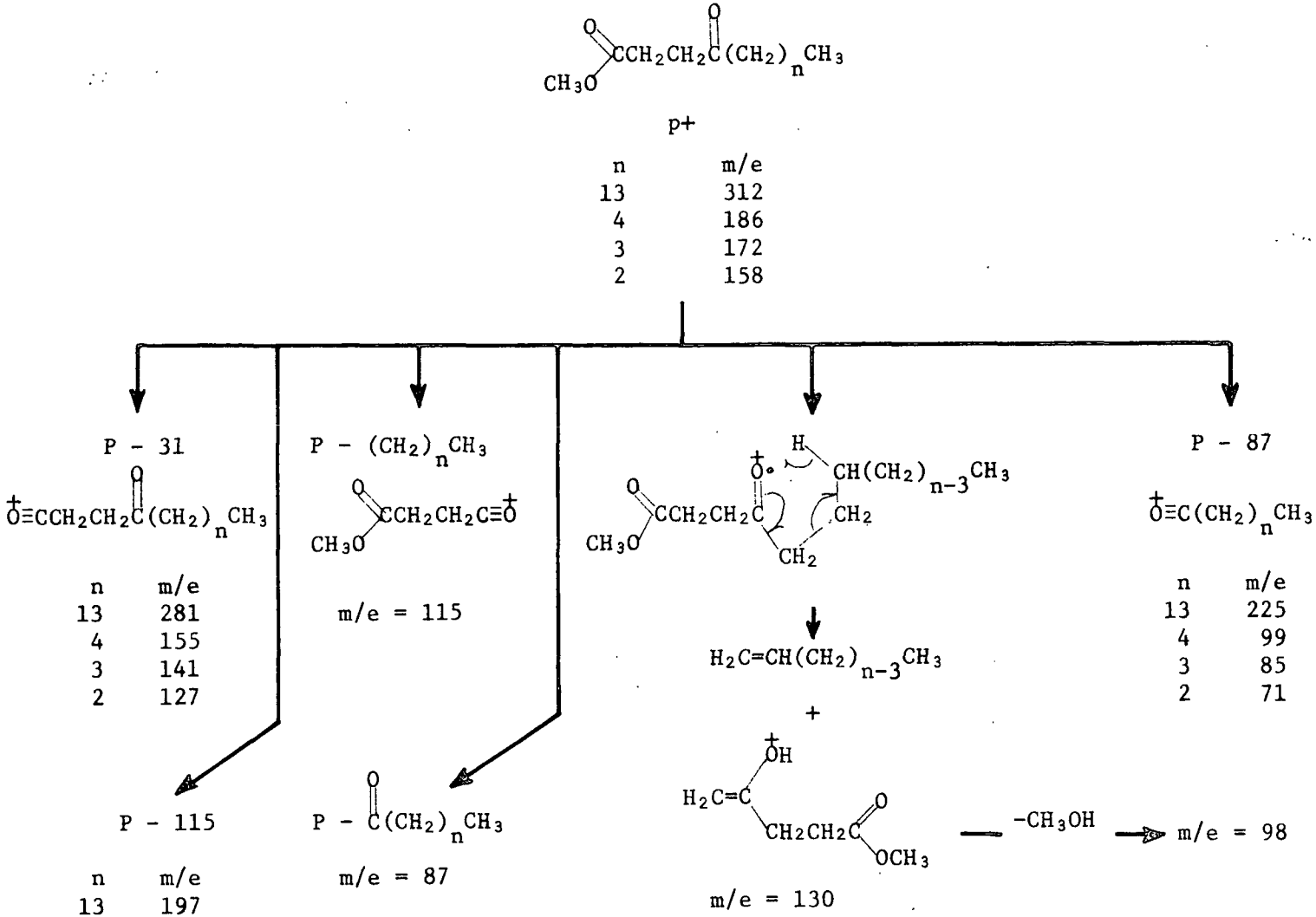


Figure 43. Fragmentation Pattern for Mass Spectra of γ-Keto Acid Methyl Esters

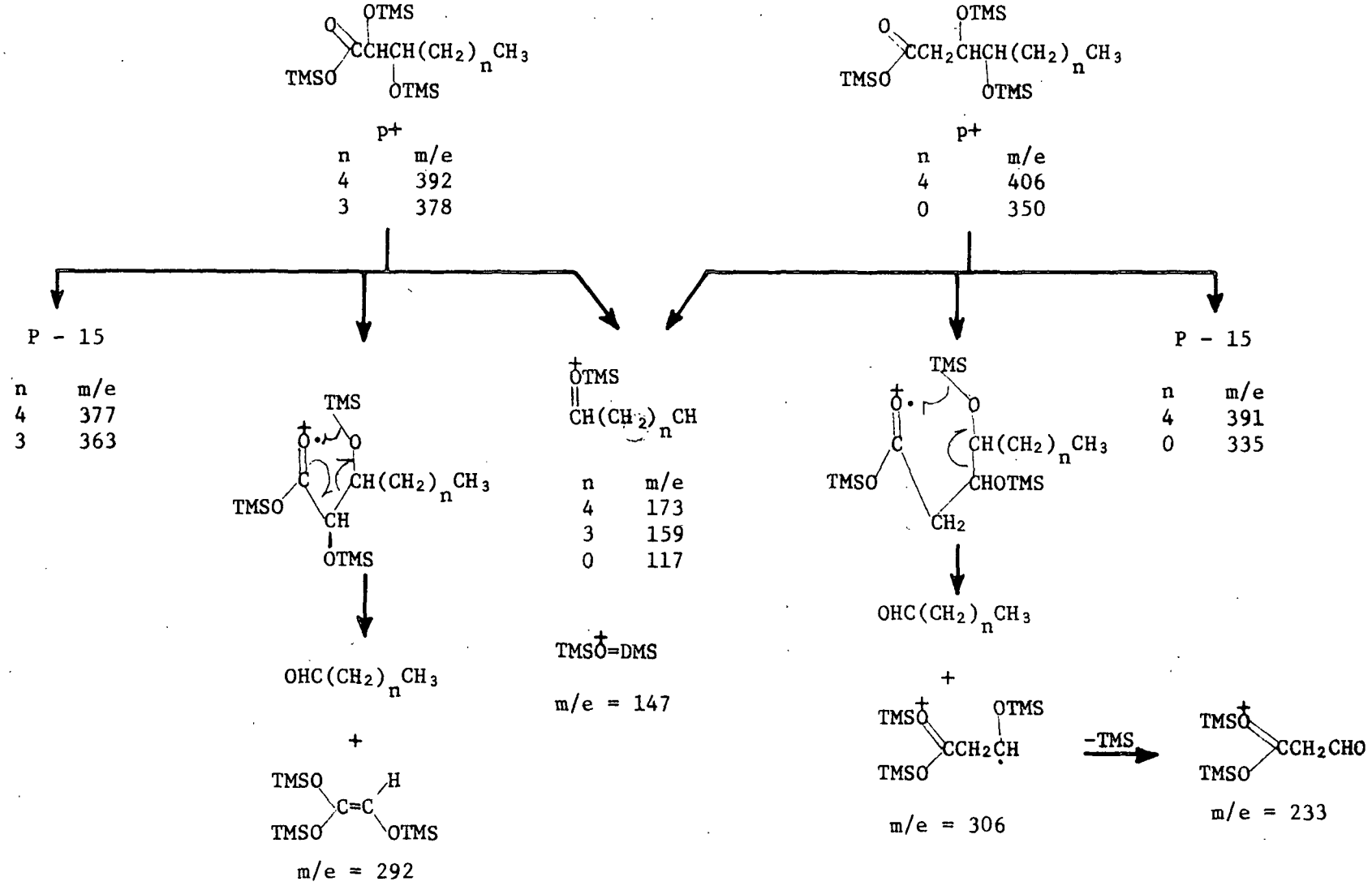


Figure 44. Fragmentation Patterns for Mass Spectra of α,β-Dihydroxy and β,γ-Dihydroxy Acid Trimethylsilyl Ester-Ethers

APPENDIX IX

METAL ION CONTENTS OF WOOD MEAL AND COTTON LINTERS SUBSTRATES

The metal ion contents of the wood meal and cotton linters substrates used during this investigation were measured by the Analytical Department of The Institute of Paper Chemistry. The concentration of mercury was determined by atomic absorption spectrometry, while the following elements were analyzed by emission spectrometry: manganese, iron, magnesium, copper, calcium, and cobalt. The results are presented in Table LI.

TABLE LI

METAL ION CONTENTS OF WOOD MEAL AND COTTON LINTERS

Material	Metal Ion Content (ppm)						
	Hg	Mn	Fe	Mg	Cu	Ca	Co
Wood Meal							
Before SO_2 Wash	0.13	48	26	220	1.9	540	0.11
After SO_2 Wash	N.D.	8.2	14	140	1.6	260	0.041
Cotton Linters	0.040	0.11	4.8	7.6	2.6	56	0.007

APPENDIX X

THE HALF FACTORIAL EXPERIMENTAL DESIGN

DEVELOPMENT OF THE HALF FACTORIAL DESIGN (60)

To understand development of the half factorial experimental design employed during this investigation, first consider a full factorial design for four variables, designated A, B, C and D, involving each variable at a high (+) and low (-) level. The complete design is represented by Table LII.

TABLE LII

2^4 FULL FACTORIAL DESIGN FOR FOUR VARIABLES

Reaction No.	Treatment Combination	Level of Variable			
		A	B	C	D
1	(1)	-	-	-	-
2	a	+	-	-	-
3	b	-	+	-	-
4	ab	+	+	-	-
5	c	-	-	+	-
6	ac	+	-	+	-
7	bc	-	+	+	-
8	abc	+	+	+	-
9	d	-	-	-	+
10	ad	+	-	-	+
11	bd	-	+	-	+
12	abd	+	+	-	+
13	cd	-	-	+	+
14	acd	+	-	+	+
15	bcd	-	+	+	+
16	abcd	+	+	+	+

Treatment combinations, or the levels of all variables within specific reactions, are designated according to the following system of notation (60). A variable assigned to its higher level is denoted by the lower case of the capital letter which symbolizes the variable. The absence of any symbol for a particular variable indicates that the variable is assigned to its lower level. If all of the variables are assigned to their lower levels, as in Reaction 1 of Table LII,

then the treatment combination is described by the numeral (1), showing that no variable is at its higher level. When only one variable is assigned to its higher level, as in Reactions 2, 3, 5 and 9, the treatment combination is described by one letter. Conversely, Reaction 16 is identified by the treatment combination abcd, showing that all variables are assigned to their higher levels. In the remaining reactions, two or three variables are at their higher levels, and the treatment combinations are composed of two or three letters.

Main effects of the variables, defined as the differences between average responses determined at the higher and lower levels of the variables, may be calculated from the factorial expressions (52)-(55).

$$\text{Main Effect of A} = 1/8(a - 1)(b + 1)(c + 1)(d + 1) \qquad (52)$$

$$\text{Main Effect of B} = 1/8(a + 1)(b - 1)(c + 1)(d + 1) \qquad (53)$$

$$\text{Main Effect of C} = 1/8(a + 1)(b + 1)(c - 1)(d + 1) \qquad (54)$$

$$\text{Main Effect of D} = 1/8(a + 1)(b + 1)(c + 1)(d - 1) \qquad (55)$$

The expressions shown are strictly symbolic; each equation must be expanded to show the actual treatment combinations involved in the calculation. For example, the main effect of Variable C, represented by Equation (54), takes the form of Equation (56) when expanded.

$$\text{Main Effect of C} = 1/8(c + ac + bc + abc + cd + acd + bcd + abcd) - 1/8((1) + a + b + ab + d + ad + bd + abd) \qquad (56)$$

Each of the treatment combinations in Equation (56) is correlated to one of the reactions listed in Table LII. To determine the main effect of C, the average response of Reactions 1-4 and 9-12 ((1), a, b, ab, d, ad, bd, abd) is subtracted from the average response of Reactions 5-8 and 13-16 (c, ac, bc, abc, cd, acd, bcd, abcd). Note that in Reactions 1-4 and 9-12 the Variable C is assigned to its

lower level, while in Reactions 5-8 and 13-16 it is at its higher level. Expansions of Equations (52), (53) and (55) yield expressions analogous to Equation (56) for the other three main effects. Equations (52)-(55) may be generalized for any full factorial design containing n variables as shown below:

$$\text{Main Effect of A} = 1/8(a - 1)(b + 1).....(n + 1)$$

$$\text{Main Effect of B} = 1/8(a + 1)(b - 1).....(n + 1)$$

$$\vdots$$

$$\text{Main Effect of N} = 1/8(a + 1)(b + 1).....(n - 1)$$

In each case, the equation must first be expanded before the actual calculation of the main effect can be conducted.

In a 2^4 full factorial design (Table LII) two factor interactions are calculated from the expanded forms of Equations (57)-(62).

$$\text{Interaction AB} = 1/8(a - 1)(b - 1)(c + 1)(d + 1) \quad (57)$$

$$\text{Interaction AC} = 1/8(a - 1)(b + 1)(c - 1)(d + 1) \quad (58)$$

$$\text{Interaction AD} = 1/8(a - 1)(b + 1)(c + 1)(d - 1) \quad (59)$$

$$\text{Interaction BC} = 1/8(a + 1)(b - 1)(c - 1)(d + 1) \quad (60)$$

$$\text{Interaction BD} = 1/8(a + 1)(b - 1)(c + 1)(d - 1) \quad (61)$$

$$\text{Interaction CD} = 1/8(a + 1)(b + 1)(c - 1)(d - 1) \quad (62)$$

A two factor interaction between any two variables is defined as the difference between the effect of either one of the variables determined at the higher level of the other, and its effect as determined at the lower level of the other variable. Again, the factorial expressions (57)-(62) must first be expanded to give the actual treatment combinations involved in the calculation of the interactions.

For example, the two factor interaction between A and C [Equation (58)] takes the form of Equation (63) when expanded.

$$\text{Interaction AC} = 1/8(abcd + abc + acd + ac + bd + b + d + (1)) - 1/8(abd + ab + ad + a + bcd + bc + cd + c) \quad (63)$$

Thus, the two factor interaction AC is calculated by subtracting the average response of Reactions 2, 4, 5, 7, 10, 12, 13 and 15 (treatment combinations a, ab, c, bc, ad, abd, cd, bcd) from the average response of Reactions 1, 3, 6, 8, 9, 11, 14 and 16 [treatment combinations (1), b, ac, abc, d, bd, acd, abcd]. For any full factorial design containing n variables, the two factor interactions are determined from the expanded forms of expressions analogous to Equations (57)-(62):

$$\text{Interaction AB} = 1/8(a - 1)(b - 1)(c + 1).....(n + 1)$$

$$\text{Interaction AC} = 1/8(a - 1)(b + 1)(c - 1).....(n + 1)$$

$$\vdots$$

$$\text{Interaction AN} = 1/8(a - 1)(b + 1)(c + 1).....(n - 1)$$

$$\vdots$$

$$\text{Interaction (N-1)N} = 1/8(a + 1)(b + 1).....(n-1 - 1)(n - 1)$$

Three factor interaction among any three variables of a 2^4 full factorial design are determined from the expanded forms of Equations (64)-(67), while the expanded form of Equation (68) corresponds to the four factor interaction among all the variables.

$$\text{Interaction ABC} = 1/8(a - 1)(b - 1)(c - 1)(d + 1) \quad (64)$$

$$\text{Interaction ABD} = 1/8(a - 1)(b - 1)(c + 1)(d - 1) \quad (65)$$

$$\text{Interaction ACD} = 1/8(a - 1)(b + 1)(c - 1)(d - 1) \quad (66)$$

$$\text{Interaction BCD} = 1/8(a + 1)(b - 1)(c - 1)(d - 1) \quad (67)$$

$$\text{Interaction ABCD} = 1/8(a - 1)(b - 1)(c - 1)(d - 1) \quad (68)$$

A three factor interaction among three variables is the difference between the two factor interaction of any two of them measured at the high and low levels of the third variable. Similarly, the four factor interaction among all four variables is a measure of the dependence of any three factor interaction on the level of the fourth variable. Again, Equations (64)-(68) may be written in general terms which apply to any 2^n full factorial design.

The 2^5 half factorial design finally developed was conceived by equating the four factor interaction [Equation (68)] of the 2^4 full factorial design (Table LII) with the main effect of the fifth variable. When expanded, Equation (68) assumes the form of Equation (69).

$$\begin{aligned}\text{Main Effect of E} &= \text{Interaction ABCD} \\ &= 1/8(abcd + ab + ac + ad + bc + bd + cd + (1)) \\ &\quad - 1/8(a + b + c + abc + d + abd + acd + bcd) \qquad (69)\end{aligned}$$

Thus, the interaction is determined by subtracting the average response of Reactions 2, 3, 5, 8, 9, 12, 14 and 15 (treatment combinations a, b, c, abc, d, abd, acd, bcd) from the average response of Reactions 1, 4, 6, 7, 10, 11, 13 and 16 (treatment combinations (1), ab, ac, bc, ad, bd, cd, abcd).

To equate interaction ABCD with the effect of the fifth variable, E, that variable was assigned to its higher level in the latter eight reactions (1, 4, 6, 7, 10, 11, 13 and 16) and to its lower level in the other eight (2, 3, 5, 8, 9, 12, 14 and 15). The four factor interaction of the original 2^4 full factorial design was assumed to be zero, and the actual quantity calculated from Equation (69), after inclusion of the fifth variable, represented only the main effect of that variable. The modified plan, a 2^5 half factorial design for five variables, is shown in Table LIII, which is equivalent to the design shown in Table V.

Treatment combinations incorporating the fifth variable are correlated to treatment combinations of the original full factorial design in the table.

TABLE LIII

2^5 HALF FACTORIAL DESIGN FOR FIVE VARIABLES

Reaction No.	Treatment Combination	Level of Variable A	B	C	D	E
1	(1) = e	-	-	-	-	+
2	a = a	+	-	-	-	-
3	b = b	-	+	-	-	-
4	ab = abe	+	+	-	-	+
5	c = c	-	-	+	-	-
6	ac = ace	+	-	+	-	+
7	bc = bce	-	+	+	-	+
8	abc = abc	+	+	+	-	-
9	d = d	-	-	-	+	-
10	ad = ade	+	-	-	+	+
11	bd = bde	-	+	-	+	+
12	abd = abd	+	+	-	+	-
13	cd = cde	-	-	+	+	+
14	acd = acd	+	-	+	+	-
15	bcd = bcd	-	+	+	+	-
16	abcd = abcde	+	+	+	+	+

In the design presented, the four factor interaction of Variables A, B, C and D is confounded (equated) with the main effect of Variable E, as was explained. A more thorough examination of the design will shown that the main effect of any variable is confounded with the four factor interaction among the other four variables. The design may thus be considered a 2^4 full factorial design for any four of the variables, in which their four factor interaction is confounded with the main effect of an added fifth variable. Furthermore, the three factor interactions of all variables, calculated from the expanded forms of Equations (64)-(67), are all equated with the two factor interactions between those variables not involved in the three factor interactions. For example, the two factor interaction between A and E is calculated from Equation (67), which corresponds to the three factor interaction BCD of the 2^4 full factorial design. In the half factorial design, which includes a fifth variable but the same number of

experiments, the three factor interaction, BCD, is assumed to be zero. The two factor interaction, AE, is calculated from the expanded form of Equation (67), represented by Equation (70).

$$\text{Interaction AE} = \text{Interaction BCD}$$
$$= 1/8(b + ab + c + ac + d + ad + bcd + abcd)$$
$$- 1/8((1) + a + bc + abc + bd + abd + cd + acd) \qquad (70)$$

The treatment combinations comprising Equation (70) are correlated to the treatment combinations of the half factorial design as shown in Table LIII. Thus, interaction AE is calculated by subtracting the average response of Reactions 1, 2, 7, 8, 11, 12, 13 and 14 (treatment combinations e, a, bce, abc, bde, abd, cde, acd) from the average response of Reactions 3, 4, 5, 6, 9, 10, 15 and 16 (treatment combinations b, abe, c, ace, d, ade, bcd, abcde). The other two-factor interactions involving Variable E are determined similarly, and each of them is confounded with a three factor interaction. The two factor interactions involving only Variables A, B, C or D are calculated from the expanded forms of Equations (57)-(62), but each of those interactions is confounded with a three factor interaction involving Variable E and two other variables. To determine the two factor interactions, all three factor interactions are assumed to be negligibly small.

For a more thorough discussion of factorial and fraction factorial experimental designs, the reader is referred to Chapters 7-10 of Davies (60).

ANALYSIS OF VARIANCE FOR THE HALF-FACTORIAL EXPERIMENTAL DESIGN (60,64)

To test the significance of main effects and interactions, mean squares were calculated for all of them. Main effects and interactions were determined

independently for the yields of oleate and linoleate, and they were presented in Table X. The mean squares derived for each effect and interaction were listed in Tables VIII and IX. The sum of squares for each main effect was calculated according to Equation (71).

$$\text{Main Effect Sum of Squares for Variable u} = 8\left[\sum_{i=1}^{2}\left(\frac{\Sigma Y_{ui}}{8} - \frac{\Sigma Y}{16}\right)^2\right] \qquad (71)$$

where ΣY = sum of yields of oleate or linoleate over all reactions

ΣY_{ui} = sum of yields of oleate or linoleate in all reactions involving Variable u at level i

For a factorial design involving sixteen experiments, the sums of squares represented by Equation (71) are mathematically equivalent to the squares of the main effects themselves, multiplied by a factor of 4 as shown by Equation (72).

$$\text{Main Effect Sum of Squares for Variable u} = 4(E_u)^2, \qquad (72)$$

where E_u is the main effect of Variable u.

The sum of squares for any two factor interaction between two variables, u and v, is defined by Equation (73).

$$\text{Interaction Sum of Squares for Variables u and v} = 4\left[\sum_{i=1}^{2}\sum_{j=1}^{2}\left(\frac{\Sigma Y_{ui,vj}}{4} - \frac{\Sigma Y_{ui}}{8} - \frac{\Sigma Y_{vj}}{8} + \frac{\Sigma Y}{16}\right)^2\right] \qquad (73)$$

where $\Sigma Y_{ui,vj}$ = sum of yields of oleate or linoleate for all reactions involving Variable u at level i and Variable v at level j

ΣY_{ui} = sum of yields of oleate or linoleate for all reactions involving Variable u at level i

ΣY_{vj} = sum of yields of oleate or linoleate for all reactions involving Variable v at level j

ΣY = sum of yields of oleate or linoleate over all reactions

As with the main effect sums of squares, the interaction sums of squares represented by Equation (72) are mathematically equivalent to the squares of the interactions themselves, multiplied by a factor of 4 as shown in Equation (74).

$$\text{Interaction Sum of Squares for Variables u and v} = 4(I_{uv})^2, \qquad (74)$$

where I_{uv} is the interaction between Variables u and v.

Because each main effect and each interaction is associated with one degree of freedom, each main effect sum of squares and each interaction sum of squares is equivalent to its mean square, as was shown in Tables VIII and IX.

Derivations of the error mean squares (EMS) for the yields of oleate and linoleate are summarized in Tables LIV and LV, respectively. The error mean squares were computed from the results of Reactions 17F-21F. The significance of each main effect and interaction was tested by dividing its mean square by the error mean square, and checking that ratio against the value listed in the F-distribution tables (60) for the appropriate significance level and degrees of freedom.

TABLE LIV

OLEATE ERROR MEAN SQUARE

Reaction No.	Percent Yield, x	Mean Percent Yield $\bar{x}$	$(x - \bar{x})^2$	Squares	Degrees of Freedom	Mean Square
17F	54.1		75.69			
18F	68.6	62.8	33.64	117.7	2	
19F	65.7		8.41			
20F	40.7	43.3	6.76	13.5	1	
21F	45.9		6.76			
		Total Sum of Squares =		131.2	3	43.7 (EMS)

TABLE LV

LINOLEATE ERROR MEAN SQUARE

Reaction No.	Percent Yield, $\bar{x}$	Mean Percent Yield, $\bar{x}$	$(x - \bar{x})^2$	Sum of Squares	Degrees of Freedom	Mean Square
17F	34.9		114.49			
18F	52.4	45.6	46.24	175.9	2	
19F	49.5		15.21			
20F	30.7	32.1	1.96	3.9	1	
21F	33.5		1.96			
		Total Sum of Squares =		179.8	3	59.5 (EMS)